THE HYDROGENATION OF OILS

CATALYZERS AND CATALYSIS

AND

THE GENERATION OF HYDROGEN

BY

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PREFACE

The course of development of the oil industry is marked by the milestones of discovery, embracing glycerine recovery, hydrolytic saponification, the Twitchell process, the distillation of fatty acids, the Wesson process of oil deodorization, the pioneer work of Mège Mouries and the resulting margarine industry, the intimate incorporation of oil and stearin by sudden chilling to form lard compound, the desulfurization of petroleum oils by copper oxide; and to the foregoing should be added a comparatively recent discovery, the technical hydrogenation of oils, which is destined to take a very prominent place in the oil industry. The extensive use of the hydrogenation process is beyond doubt; it must in fact be regarded as the most important advance in the technology of oils during recent years. The probable effect on the oil and allied industries and on the oil and oil seed markets is difficult to forecast, as the full possibilities of the process cannot yet be determined.

The whole structure of hydrogenation resides in the catalytic action of practically only a limited number of metals and their compounds, which awaken the usually passive element hydrogen from its dormant condition and thus enable its combination with unsaturated bodies. Often the term catalysis is said to be an overworked expression under cover of which chemists may find refuge when pressed for an explanation of obscure phenomena. But whether or not the term is overworked it is indeed certain that with rational treatment catalyzers are the hardest workers in the domain of chemistry and may effect the transformation of a prodigious amount of raw material without detriment to themselves unless perchance their labors are checked by the accidental presence of certain unfriendly bodies or catalyzer "poisons" as these are termed.

In 1823 Dobereiner found that hydrogen would ignite, when, in the presence of air, it was exposed to finely-divided platinum, and this manifestation of catalytic activity by platinum and also palladium was studied during the middle of the last century by Liebig, Debus and others. In 1888 Mond made use of reduced nickel on a porous carrier, curiously enough not to add hydrogen but to eliminate it, thus providing a method of preparing hydrogen gas. Ten years or

so later, Sabatier and Senderens reversed this procedure and made such nickel carry hydrogen to unsaturated organic compounds of a character which could be vaporized readily. Then in 1903 came Normann who disclosed the application of nickel catalyzer to the hydrogenation of fixed or fatty oils or the production of stearin from olein. But it was years afterwards before the idiosyncrasies of catalytic nickel were fully understood and the technical difficulties of hydrogenation were surmounted so as to afford eminently practical results.

To-day this branch of the oil industry is growing by leaps and bounds and its advent into the field has brought a flood of congratulations, protests and criticisms, market disturbances, and great activity among chemists to improve the catalytic materials and processes of treatment involved.

The present book it is hoped will be of assistance to the practical worker as well as to the student of oils and fats. It has been the outgrowth of a number of years of observation and experience involving the collection of a considerable amount of data from many sources. An attempt was made by the author to present the matter in brief form before the Society of Chemical Industry in 1912 and the present volume is based on the general plan or arrangement of material adopted in that paper.

Heretofore, the literature on hydrogenation has been scattered through many periodicals and no effort has been made to collect this material and arrange it in book form, although the treatises of Hefter and Ubbelohde and Goldschmidt include a few pages on the conversion of soft fats by various methods to stearic acid or stearin; but such reviews have been too brief to afford the practical operator sufficient working material.

A considerable mass of data including practically all that has been advanced on the subject of hydrogenation of fatty oils has been collected and arranged in this volume. The observations and opinions of many minds have been brought together. Some of these views obviously are sound, others are open to grave doubt and still others are of a contradictory or polemical nature. Whether or not in the treatment of this material to carry through a vein of critical comment was a problem which confronted the author and the conclusion was reached that at this stage of a young art, it would be inadvisable in general to do more than array the multitude of processes, formulæ proposals and opinions, leaving to the reader the selection of that which should prove of greatest utility.

A few years hence when oil hydrogenation will have found its measure and the more important points concerning it have reached

definite settlement, the allotment of space to a number of the discussions appearing on the following pages would hardly be warranted, but at the present time when many are desirous of having at hand a treatise which comprises all or nearly all the published work to date, containing though it does a considerable divergency of opinion, there appears ample justification for the inclusion of material which later may be considered superfluous.

Frequent reference has been made to the material scattered through the literature and acknowledgment is rendered to these sources of information, especially to the Journal of the Society of Chemical Industry and the Seifenseider Zeitung.

C. E.

MONTCLAIR, N. J.
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THE HYDROGENATION OF OILS

CHAPTER I

METHODS OF HYDROGENATION

For years the dream of the oil chemist was to find a solution to the problem of converting oleic acid into stearic acid, or olein into stearin, simply by the addition of hydrogen, so as to make valuable hard fats from relatively cheap raw material. Superficially the problem looked simple. Oleic acid is the next door neighbor of stearic acid, apparently differing only in having a little less hydrogen than stearic acid has in its constitution. Only a trifling amount of hydrogen, less than one per cent, is required to transform oleic into stearic acid.

But the problem was far from simple as oleic acid stubbornly resisted the invasion of hydrogen into its structure to any material extent under the earlier methods of hydrogen addition, and not until recent years, with the discovery of effective hydrogen carriers or catalyzers, has it become possible to bring about this conversion economically with large yields so as to warrant commercial exploitation in an extensive way.

Now the problem is solved, and in different parts of the globe dozens of plants turning out daily enormous quantities of "hardened oil" prepared by the treatment of vegetable or other oil with hydrogen have been established.* So eagerly has the oil handling world lent itself to the idea that already the stearin market has lost its firmness and much speculation is rampant as to the nature of price readjustments which perhaps are on the way. Unquestionably hydrogenated or hardened oil has taken its place in the oil market as a staple product.

A Review of the Art.†‡

Many attempts to hydrogenate oleic acid have been made. Reviewing this subject in 1897 § **Lewkowitsch** refers to the ease with

* A list of over twenty firms in different parts of the world having plants for hardening oils is found in Seifensieder Zeitung, 1914, 349.

† See Ellis, J. S. C. I., 1912, 1155; J. Ind. Eng. Chem., 1913, 95; The American Perfumer, 1913.

‡ The production of stearic acid and other acids or products of high melting point from oleic acid is discussed by Hefter, Technologie der Fette und Öle, Vol. III, 795 and 994; also by Ubbelohde und Goldschmidt, Handbuch der Chemie und Technologie der Öle und Fette, Vol. III, 152.

§ J. S. C. I., 389 (1897).

which the lower members of the oleic series are converted into saturated acids and states that "oleic acid itself resists all attempts at hydrogenization," further remarking that he had "carried out a large number of experiments in this direction under most varied conditions, but hitherto all of these gave negative results."

Prior to this, however, **Goldschmidt,** in 1875,* had reduced oleic acid by means of hydriodic acid and amorphous phosphorus at 200° to 210° C. This presumably led to the attempted commercial development of a process by **de Wilde and Reychler**† involving heating oleic acid to 280° C. with 1 per cent of iodine, adding and melting therein a certain quantity of tallow soap, and then boiling with acidulated water. The product was then distilled and the iodine, in part, recovered from the pitch. The yield of stearic acid or saturated fat is stated to be approximately 70 per cent of the theoretical. Only about two-thirds of the iodine could be recovered so the process apparently did not find technical use.‡ Should the much lauded method of treating kelp, primarily for obtaining potash salts, come into use, a cheap supply of iodine would be available which might then make the Wilde and Reychler process of some technical interest.

Chlorine in lieu of iodine has been tried, but great difficulty has been experienced in securing an autoclave of resistant material. **Imbert** § recommends using quantities of chlorine and alkali exactly calculated on the iodine number of the fatty acid and operating at a temperature of 120° to 150° C. and a pressure of about five atmospheres for a period of six hours.

Zurrer ‖ chlorinates the fatty acid and then heats with water in the presence of a finely-divided metal, as zinc or iron. Lewkowitsch alleges that the treatment of monochlor-stearic acid in this manner causes a reversion to oleic acid.

Tissier, in 1897,¶ lays claim to a process for the reduction of oleic acid by nascent hydrogen. Powdered metallic zinc is placed in an autoclave, water and the fatty material containing olein being introduced, and treated under pressure.

Under the circumstances the glyceride is hydrolyzed to fatty acid and glycerine, and according to Tissier nascent hydrogen is evolved by

* Sitz. b. d. Wiener Akad. d. Wiss., 72, 366.

† Bull. Soc. Chim. [3], 1, 295 (1889).

‡ Chem. Ztg., 1889, 595.

§ U. S. Patent No. 901,905, October 20, 1908; see also Bull. Soc. Chim., 1899, 695, 707.

‖ German Patent No. 62,407, August 8, 1891.

¶ French Patent No. 263,158, January 16, 1897.

virtue of the finely-divided metal and reduces the oleic to stearic acid. **Freundlich** and **Rosauer** * claim the Tissier process to be inoperative.

The conversion of oleic acid into palmitic and acetic acids by means of caustic potash in accordance with the **Varentrapp** reaction † has not proved to be of much commercial significance, although it appears that certain firms have been making use of the process in a limited way.

The **Schmidt** zinc chloride process‡ involves heating oleic acid and zinc chloride at exactly 185° C. while interaction is taking place. " Deviation from this point leads to an increase of liquid substance. Unfortunately the solid candle material must be distilled and the considerable proportion of β-hydroxy-stearic acid (melting point 82° C.) in the crude product is seriously diminished by the partial conversion of this acid into oleic and iso-oleic acids. Thus, from a candle-maker's point of view, a substance of high melting point is rendered practically valueless. Schmidt's process was tried on the large scale in an Austrian candle works. The quantity of liquid *unsaponifiable* substance obtained was, however, so large that commercial success was out of the question."

Many processes based on the well-known action of sulfuric acid on oleic acid have been proposed. Hydroxy-stearic acid is obtained by steaming the product. It would lead us too far from the present subject to enter into any further discussion of these reactions.

Processes Involving Application of Electricity

In 1886 **Weineck** § called attention to the possibility of electrolytic addition of hydrogen to oleic acid. **Kuess** ‖ later attempted to apply the electric current in the steam distillation of fatty acids.

In patents taken out by **Magnier, Bragnier** and **Tissier,**¶ the fatty material is acidified with sulfuric acid, whereupon the acidified mass is mixed with 5 to 6 times its weight of water and then under a pressure of 5 atmospheres is subjected to the action of an electric current, which generates hydrogen in a nascent state.

An interesting method of converting oleic into stearic acid is that comprised in the **Hemptinne** electric discharge process. The method

* Chem. Ztg., 1900, 566.

† J. S. C. I., 98 (1883), 200 (1884).

‡ Lewkowitsch, "Oils, Fats and Waxes," p. 664.

§ Osterr. Privil., 10, 400 (July 19, 1886).

‖ Chem. Ztg., 1896, 618.

¶ British Patent 3363, 1900; German Patent 126,446, October 3, 1899, and additional German Patent 132,223.

is carried out by interposing a thin layer of the oil in the path of an electric discharge, while bringing hydrogen into contact with the oil.*

Fig. 1 shows the arrangement of apparatus for this purpose. The conversion is effected in a chamber having an inlet pipe *H*, furnishing hydrogen under constant pressure. Oleic acid is supplied by a pipe *O* to a sprinkling device which discharges the acid onto a system of parallel plates consisting of the glass plates *G* and alternately the metal plates *M*, *N*. The metal plates *M* are connected to one pole, the others, *N*, being connected with the other pole of a source of electricity.

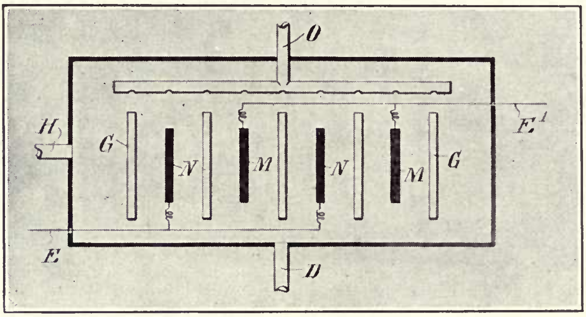


Fig. 1.

As the oil passes over the plates the electrical discharge causes conversion of some oleic acid into stearic acid, and analogous compounds having melting points in the neighborhood of 69° C.

Hemptinne prefers to work at pressures less than atmospheric. The yield is lower at atmospheric pressure. By treatment in this manner it is not difficult to secure a yield of 20 per cent of stearic acid. Repeated treatment permits even up to about 40 per cent yield. Here, as so often elsewhere, the effect of mass action becomes manifest and as the content of stearic acid increases the speed of reaction greatly decreases. Much better results are obtained by saturating to the extent of about 20 per cent, removing the stearic acid by pressing, when the oil of reduced stearic acid content is again subjected to the electric discharge, and a further 20 per cent yield obtained. The oleic residue contains liquid condensation products amounting to about 40 per cent of the total weight. It is stated that the presence of these bodies does not impair the market value of what some one has termed " electrocuted " oleic acid.

* U. S. Patent 797,112, August 15, 1905.

Petersen * also endeavored to reduce oleic acid to stearic acid by allowing an electric current to act between nickel electrodes on an alcoholic oleic acid solution, slightly acidulated with sulfuric acid or preferably with hydrochloric acid. But the yield of stearic acid was small, even under the most favorable conditions, and did not exceed 15 to 20 per cent.

Petersen also endeavored to reduce sodium oleate in aqueous or alcoholic solution to the stearate. No satisfactory results were obtained.

C. F. Böhringer and Sohne † obtained by the same method much better results when using as cathodes, metallic electrodes, which were covered with a spongy layer of the same metal. They recommend as cathodes platinized platinum, and also palladium electrodes covered with a spongy layer of palladium-black. Nickel electrodes are not as effective.

Bruno Waser ‡ states that oleic acid or olein should be sulfonated and freed from free sulfuric acid before adding hydrogen electrically (cathodic reduction). As an example, one equivalent of oleic acid is mixed with two or three equivalents of 95 per cent sulfuric acid, the temperature not being permitted to advance more than 5 degrees. The mixture is allowed to stand 24 hours, is then washed with ice cold water and dissolved in boiling water. This solution serves as catholyte, a 30 per cent sulfuric solution being the anode liquid. A diaphragm separates lead electrodes. The temperature is maintained at 90° to 100° C. with a current density of 25 to 100 amperes per square decimeter, giving 60 to 70 per cent conversion to stearic acid.

Hydrogenation by Catalytic Action

Kolbe § in 1871 states that **Saytzeff** reduced nitrobenzol to aniline by passing the vapors of the former, mingled with hydrogen, over palladium-black.

About twenty-five years later **Sabatier and Senderens** began their classic study of nickel and other metallic catalyzers.

The work of Sabatier and Senderens ‖ laid the foundation for the

* Z. Elektrochemie, 1905, 549.

† German Patents 187,788, 189,332, 1906.

‡ German Patent 247,454, March 24, 1911, and Seifen. Ztg., 1912, 661.

§ J. prakt. Chem. [2], 4, 418 (1871).

‖ Sabatier and Senderens published the results of their earlier work in Comp. rend., **132**, 210, 566 and 1254. A very complete description of their investigations appears in Ann. de Chim. et de Phys., 1905 (8), **4**, 319–488. See also Mailhe Chem. Ztg., 1907 (31), 1083, 1096, 1117, 1146 and 1158; Chem. Ztg., 1908 (32), 229 and

present processes of hydrogenation of oils. These distinguished chemists first recognized the effectiveness of nickel and certain other metals as carriers of hydrogen and they elaborated a series of brilliant experiments extending over a number of years, which demonstrated that unsaturated compounds, that is, bodies lacking in hydrogen, could be saturated or given the full quota of hydrogen by contact with this gas in the presence of a catalyzer or carrier, such as finely-divided nickel. By their painstaking labors the reaction was shown to be one of general application.

Fig. 2 shows the apparatus used by these investigators in the hydrogenation of bodies capable of vaporization. In this apparatus, 1 is

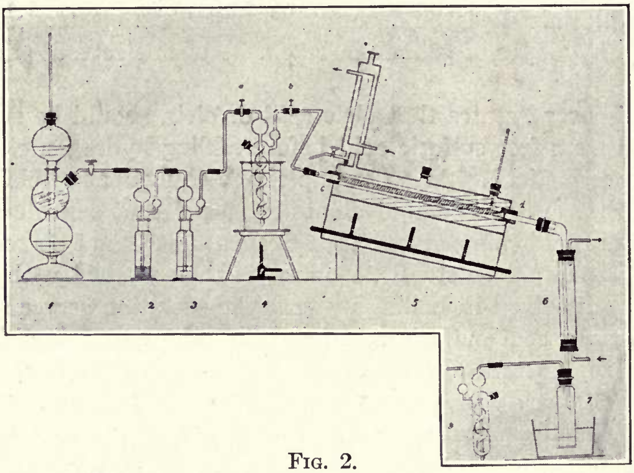


FIG. 2.

a hydrogen generator; 2 and 3 are wash bottles; 4 is a vaporizer containing the substance to be converted into a vapor; 5 is a hydrogen chamber containing nickel catalyzer and heated by an oil bath; and 6 is a condenser.

While a good deal of work has been done on the hydrogenation of fatty oils, the literature on the subject is not very profuse and only through the patents which have been issued can we gather from any

244; Willstätter and Mayer, Ber., 1908 (41), 2199; Paal and Amberger, Ber., 1905 (38), 1406 and 2414: Paal and Gerum, Ber., 1907 (40), 2209; 1908 (41), 813 and 2273; 1909 (42), 1553; Paal and Hartmann, Ber., 1909 (42), 2239; Paal and Roth, Ber., 1908 (41), 2282; 1909 (42), 1541; Ipatiew, Ber., 1902 (35), 1047; 1904 (37), 2961; Chem. Centralbl., 1906, II, 86; Ber., 1907 (40), 1270 and 1286; 1908 (41), 991; 1909 (42), 2089, 2092 and 2100; Ipatiew, Jakowlew and Rakitin, Ber., 1908 (41), 996; Ipatiew and Philipow, Ber., 1908 (41), 1001; Padoa and Carughi, Chem. Centralbl., 1906, II, 1011.

published records much that is enlightening as to some of the technical developments in this industry. The patents concerned with the matter have, moreover, been subjected to a great deal of scrutiny because of the alleged basic character of certain of them. For these reasons the remainder of this chapter pertains very largely to processes which have been covered by patents * in this country or abroad.†

A German Patent 139,457, of July 26, 1901, to **J. B. Senderens,** is probably the first patent record having to do with the reduction of organic bodies by hydrogen in the presence of nickel catalyzers. This patent is for the production of aniline from nitrobenzol and involves passing the latter body in the form of a vapor over heated nickel, copper, cobalt, iron or palladium in the presence of hydrogen. The hydrogen may be in the pure state or in the form of water-gas.

The first disclosure of the possibility of hydrogenation of oils in a liquid state apparently comes from **Leprince** and **Siveke.**‡ In England a corresponding patent 1515, of 1903, was issued to Normann § and the latter patent has become widely known because of its alleged fundamental character.‖

* Sachs (Zeitsch. f. angew. Chem., 1913, No. 94, 784) reports 183 patents on oil hardening of which there are 33 German; 22 French; 51 English; 33 United States; 9 Belgium; and 35 in other countries.

† The illustrations immediately following are largely derived from the drawings of patent records or have been prepared from written descriptions. In some cases all details deemed unnecessary in the portrayal of the essential features of these processes have been omitted. The original records should, of course, be consulted for details. — *Author.*

‡ German Patent 141,029, August 14, 1902, Herforder Maschinenfett und Oelfabrik.

§ This English patent is owned by a large soap manufacturing house in England and has been passed on unfavorably by the courts. See Appendix.

‖ The Seifensieder Zeitung (1913), 1272, states that German Patent 141,029 (Leprince and Siveke) is controlling in that country so far as the use of metallic catalyzers for oil hardening is concerned, because this patent makes the first disclosure of the hydrogenation of bodies in the liquid state by simple addition of a catalyzer and introduction of hydrogen. According to the same journal (1913), 1195, the Bremen-Besigheimer Ölfabriken in Bremen has a large plant for the hydrogenation of fats and oils which at one time was not in use because of patent disputes between this concern and the Germania Company. The Bremen Company has made arrangements with the patent owners and is now operating the Bremen plant. (Seifen. Ztg. (1913), 1273.)

Leprince and Siveke (German Patent 141,029 was assigned on July 22, 1910, to Joseph Crosfield & Sons, Ltd., of England and was again assigned on August 9, 1911, to Naamlooze Venootschaap Anton Jurgen's Fabriken, Oss in Holland. The latter concern on the 10th of July, 1911 founded the Oelwerke Germania, G. M. b. H.,

at Emmerich, on the Rhine. The plant is reported to have been put into operation in the Spring of 1912 — almost ten years after the application for German patent 141,029.

The contentions of Professor Erdmann (Seifen. Ztg. (1914), 32) present certain points of interest. Referring to German Patent 141,029 which was applied for in 1902 and granted in 1903, Erdmann states that eight years later — without being used regularly on a large scale in Germany — the rights were sold in England to Crosfield & Sons. The requirements for the successful hardening of oils by the use of metallic nickel as a catalyst are regarded as having been here given for the first time.

The German patent application B. 62,366, IV, 12°, of Bedford, Erdmann and Williams for hydrogenating oils with the aid of metallic oxides, was entered on March 16, 1911, together with the English priority of Dec. 20, 1910, a time therefore when the Germania Werke did not exist. In addition, it is stated, Bedford and his colleagues immediately started in to actually materialize their original discoveries and ideas on a large scale; their experimental plant had been working for a considerable period and in Germany at that time oils had not been hardened on a manufacturing scale.

It is not true, Erdmann states, that the process of German patent 141,029 was the first solution of the problem of the direct addition of hydrogen to unsaturated fatty bodies. It does not cover the direct addition of hydrogen — a process for the direct addition of free hydrogen by means of a catalyst involves a contradiction of terms — but aims at the indirect addition to an unsaturated fatty substance by means of a catalytic hydrogen carrier in just the same way as this had already been accomplished previously by Karl Peters (Monatshefte f. Chemie, 1886 [7], 552), and Reformatoky (J. prakt. Chemie N. S., 1890 [41], 437) in the hydrogenation of oleic acid to stearic acid by the use of iodine as the hydrogen carrier.

At the time of the application for German patent 141,029 — that is, in 1902 — Erdmann observes that the transformation of unsaturated compounds contained in liquids to saturated compounds by means of the introduction of free hydrogen into the liquid with the aid of a catalyst was not entirely unknown. For example, in 1873, Saytzeff (in Kolbe's laboratory) obtained aminophenol and methylamin by the introduction of free hydrogen into a solution of nitrophenol or nitromethane in the presence of finely-divided palladium. (See J. prakt. Chemie. N. S. [6], 128.) In practically the same way, oleic acid could be changed to stearic acid as Fokin later showed (Chem. Centralbl. (1907), II, 1324). Hence Erdmann claims it is not true that the existence of the discovery represented by German patent 141,029 can be looked upon as the first time that a means was found to saturate unsaturated substances in the liquid state by means of free hydrogen.

In case any discovery can be found set forth in Patent 141,029 — which according to the statements of the English courts is at least very questionable — the new idea, Erdmann contends, can only be that the two steps:

(*a*) Hydrogenation of liquid *organic* substances by the introduction of free hydrogen in the presence of a finely-divided metallic catalyst, and

(*b*) Hydrogenation of unsaturated *fatty* substances in the presence of a non-metallic or not finely-divided metallic catalyst,

which steps were known separately, are combined with one another in this way, that fatty substances are hydrogenated by the introduction of free hydrogen in the presence of a finely-divided, metallic catalyst, particularly nickel which was already known to be a hydrogen carrier. Metals, also, — for example zinc — had been pro-

Normann states that he may carry out the hydrogenation of oils by treatment either in the form of vapors or as liquids. In the former case the fatty acid vapors together with hydrogen may be caused to pass over catalytic material carried by a pumice stone support. This may be represented by Fig. 3 in which *A* is a bed containing granular pumice coated with a metal catalyzer. *O* is an inlet for oil *vapors* and *H* is an inlet for hydrogen. The mixture passes through the tube *A* and the converted material is withdrawn at *B*. Normann notes, however, that it is sufficient to expose the fat or fatty acid in a liquid

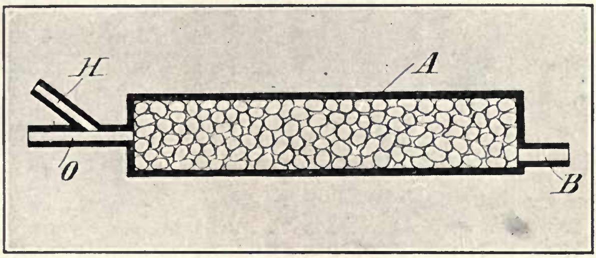


FIG. 3.

condition to the action of hydrogen and the catalytic substance. He states that, for instance, if fine nickel powder obtained by the reduction of nickel oxide in a current of hydrogen is added to oleic acid, the latter heated over an oil bath and a strong current of hydrogen caused to pass through it for a considerable time, the oleic acid may be completely converted into stearic acid.

Fig. 4 shows very simple apparatus, such as might have been used by Normann to this end. *A* is a vessel containing oil *O* in which fine particles of nickel are suspended while a strong current of hydrogen from the pipe *H* affords the hydrogen requisite for reduction of the oil. By this means Normann treated the fatty acid of tallow, having an

posed for the hydrogenation of oleic acid before 1903 (compare Tissier, Chem. Ztg., 1899 [23], 822).

Normann (Seifen. Ztg. (1913), 1381) regards the employment of metal oxides or organic salts as catalyzers to fall within the scope of the Leprince and Siveke (Normann) German patent 141,029, because of the reduction occurring when these metallic compounds are exposed to hydrogen in the hardening process. Meigen and Bartels (J. prakt. Chem. 1914, 290) support Normann's contention. The assertions of Erdmann regarding the existence of nickel suboxide when hardening oils with nickel oxide catalyzers are challenged by the Ölwerke Germania (Seifen. Ztg. 1914, 209) and it is claimed that metallic nickel forms under the conditions to which the oxide is subjected. In this connection, a brief review of Ipatieff's work is given.

iodine number of 35 and melting at about 46, thereby converting it into a body of improved color having an iodine number of about 10 and a melting point of about 58. Normann also states that commercial gas mixtures, such as water-gas, may be used in lieu of pure hydrogen.

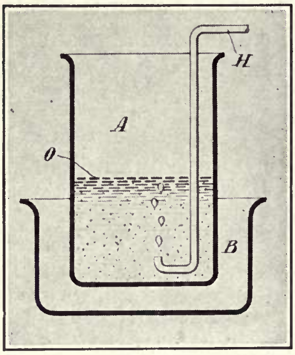


Fig. 4.

The disclosures of the Normann patent are, however, rather meagre and can hardly be considered to comprehensively traverse the difficulties encountered in the practical hydrogenation of oils in a liquid state.

Day has brought out a process * in which he treats, not fatty oils, but hydrocarbon oils, with hydrogen in the presence of what he terms a porous absorptive substance mentioning palladium black, platinum sponge, zinc dust, fuller's earth and other clays. Fig. 5 shows one method proposed by Day to this end.

The upper chamber *A* is filled with hydrocarbon oil, and porous absorptive material, such as palladium black, is introduced into the intermediate chamber *C* by way of the plugged orifice *D*. Any air present in *C* may be expelled by flushing out with hydrogen or an indifferent gas. Hydrogen is then admitted by the pipe *H* until the porous

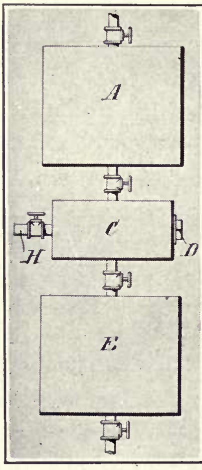


Fig. 5.

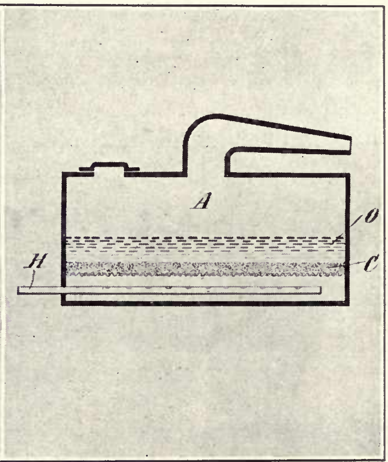


Fig. 6.

* U. S. Patent 826,089, July 17, 1906.

material has absorbed its full quota. The hydrogen gas may be admitted under a pressure of 100 pounds or more to the square inch. When the porous material in *C* has become properly charged with hydrogen, the oil is allowed to run from the chamber *A* through the chamber *C* into the collecting chamber *E*, hydrogen being introduced as required by the pipe *H*.

In the place of hydrogen, Day states that ethylene or other hydrogen-carrying gas or vapor may be employed. By this treatment the disagreeable odor of hydrocarbon oil is in great part removed and the burning qualities of the oil improved. When palladium black is used it is recommended that a proportion of one-half ounce to the gallon of oil be taken.

Fig. 6 shows a modification of Day's process. *A* is an oil still, in the lower part of which the perforated pipe *H* serves for the admission of hydrogen. Palladium black or other porous absorptive material forms a layer *C*, on a screen above the hydrogen inlet. *O* shows the charge of oil. In operating this apparatus the layer of material *C* is first charged with hydrogen and then oil run into the still. Distillation is carried out while hydrogen gas is being forced through the absorptive material and oil.*

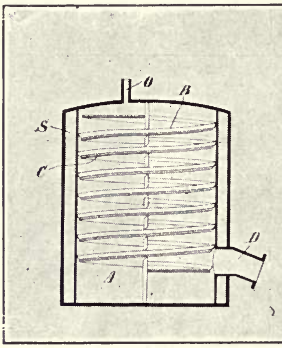
* The removal of sulfur from petroleum is effected according to Schiller (U. S. Patent 580,652, April 13, 1897), by generating hydrogen in a nascent condition in the oil during the distillation of the latter. It is claimed that sulfur is thus eliminated as hydrogen sulfide. Zinc dust and an alkaline hydrate, such as dry powdered caustic soda, are employed to generate hydrogen. These are added to the oil undergoing distillation. Huston (U. S. Patent 486,406, Nov. 15, 1892) proposes to remove sulfur by heating the vapors of a sulfur-containing petroleum oil admixed with steam to a temperature of 900° F. at which temperature it is said that the hydrogen of the water vapor unites with the sulfur, forming hydrogen sulfide. Hawes (U. S. Patent 444,833, Jan. 20, 1891) avails of the same reaction and brings a mixture of vapor of hydrocarbon and water into contact with gravel contained in a chamber which is heated to a temperature of 400° to 600° F. Dubbs (U. S. Patent 470,911, March 15, 1892) forces a gas rich in hydrogen through oil in a still to remove sulfur as hydrogen sulfide. Stevens (U. S. Patent 414,601, Nov. 5, 1889) claims steam reacts with the sulfur present in petroleum oils to form sulfurous acid, while the hydrogen thus liberated combines with the carbon of the oil, resulting in an increased yield of light oil. See also Turner (U. S. Patent 1,046,683, Dec. 10, 1912) and Noad (U. S. Patent 971,468, Sept. 27, 1910). Hall (U. S. Patent 362,672, Nov. 8, 1887) uses "converting surfaces" of granite. Wilkinson (U. S. Patent 145,707, Dec. 16, 1873) has specified the distillation of petroleum oils with hydrogen.

The French patents to Sabatier, 400,141, and to Haller, Sabatier and Senderens, 376,496, are of interest in this connection.

In studying the effects of catalytic agents upon the decomposition of petroleum oils, 100 grams of coarsely powdered porous earthenware upon which nickel had been reduced in metallic form were impregnated with 10 to 12 grams of the oil, and heated

The British Patent to **Bedford** and **Williams,** 2520, of 1907, contains probably the first published description of a method of exposing oil to the action of hydrogen by forming the oil in a spray or films in an atmosphere of hydrogen and in contact with a catalyzer of the nickel type. In this manner the patentees state they converted linseed oil into a hard fat solidifying at 53° C. Oleic acid was converted into stearic acid having a melting point of 69° C., and paraffin wax they state had its solidifying point raised 3° C. by the treatment.

A peculiar manner of treatment has been shown by **Schwoerer,*** which will be made clear by Fig. 7. The receptacle A, which is heated



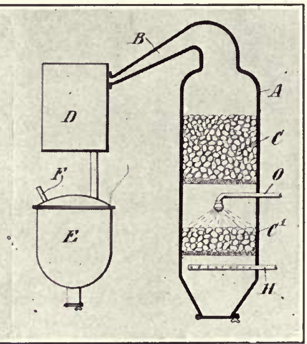


FIG. 7. FIG. 8.

by the steam jacket S, is provided with what Schwoerer calls a helical pan, shown at B. The underside of the pan carries a layer of nickelized asbestos. O is an inlet for oil and hydrogen, and D an outlet for the treated material.

Schwoerer states that he first mixes fatty acid and hydrogen by atomizing the oil with a jet of superheated steam in the presence of hydrogen and conducts this mixture through the pipe O, into the chamber A. The temperature maintained in the apparatus is from

at regulated temperatures from 180° to 500° C. in a current of hydrogen. The gases were collected and analyzed, while the distillates were compared with those obtained under parallel conditions, but without the presence of the catalytic agent. No lowering of the vapor pressure appeared to be caused by the catalytic action. Various proportions (according to the partial pressure, temperature, etc.) of hydrogen, methane, ethane and heavy hydrocarbons were produced under the influence of the catalytic agent, while the distillates were of quite different character from those yielded by the oil alone. Ubbelohde and Woronin, J. S. C. I., 1911, 1242; Petroleum 1911 [7], 9.

* U. S. Patent 902,177, Oct. 27, 1908.

250° to 270° C. Vapors of oleic acid come in contact with the layer of catalyzer on the underside of the helical pan and are converted into stearic acid. The product collects, more or less, in the gutter of the helical pan and is removed at *D*.

The repeated caution given by Sabatier to bring in contact with the catalyzer only the *vapors* of the material, doubtless led Schwoerer to devise this form of apparatus.

Bedford, presumably with the same caution of Sabatier in mind, discloses, in U. S. Patent 949,954, of Feb. 22, 1910, a process which also has to do with vaporization of the oily material. Fig. 8 shows the Bedford apparatus. A still or tower *A* carries two beds of catalyzer *C* and *C′*. This is said to be preferably nickelized pumice. By means of hydrogen under pressure, oleic acid is sprayed from the pipe *O*, onto the catalyzer bed *C′*. Hydrogen is admitted through the pipe *H*. A temperature of about 200° C. and a diminished pressure of about 50 to 100 mm. is maintained in the still or tower *A*. The vapors of oleic acid mingled with hydrogen pass through the second catalyzer bed *C*, where more or less conversion occurs, then pass to the condenser *D*, and finally collect in the receptacle *E*. *F* is a connection to a vacuum pump.

Neither this process nor that of Schwoerer is broadly applicable to the treatment of glycerides as these cannot be vaporized without undue decomposition.*

Erdmann has taken out a German Patent 211,669, of Jan. 19, 1907, involving passing an oil as spray or mist into a chamber containing nickel catalyzer supported on pumice and the like. Fig. 9 probably indicates one form suggested by Erdmann, who, by the way, does not show any drawings in the patent. The chamber *A* has a rotatable cylinder *B*, which is coated with nickel catalyzer. In the bottom of the receptacle is a quantity of nickelized pumice. Oil enters at *O* and is atomized by hydrogen entering at *H*. The atomized mixture impinges upon the rotating cylinder *B*, then passes through the bed *C*, the oil being drawn off at *D*. The excess of hydrogen is presumably vented in the upper part of the apparatus.

* Sabatier and Senderens, Annales de Chimie et de Physique [8], 4, 335 (1905), state that "Le métal ne soit jamais mouillé par un afflux excessif du liquide que l'on traite, ou a la suite d'un abaissement accidentel de la temperature du tube." They further say that in the preparation of cyclohexanol and its homologues from phenol or cresol at a temperature but slightly above the boiling points of the latter bodies, sometimes by their condensation, the nickel becomes moistened and immediately becomes almost inactive, due, no doubt, to the surface becoming permanently changed in character by contact with the liquid phenol or cresol.

A second modification (Fig. 10) involves a tower *A*, filled with catalyzer *C*, which may be in the form of nickel supported on coarse fragments of pumice. By the pipe *O* oil is admitted to the chamber in an atomized or finely-divided state. Hydrogen enters by the pipe

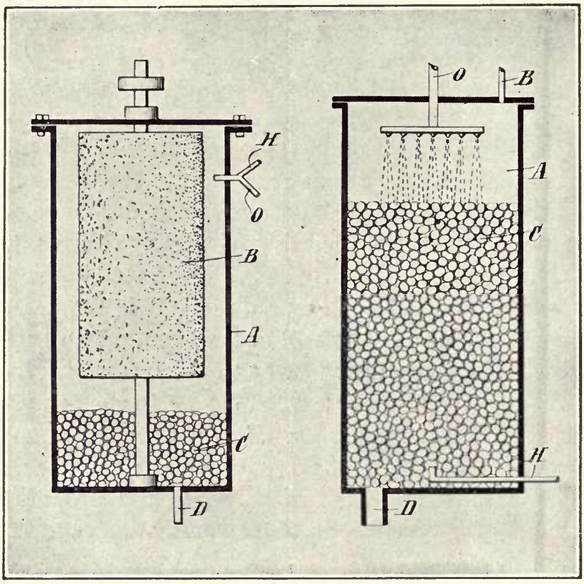


FIG. 9. FIG. 10.

H. Erdmann states that the temperature of treatment should be from 170° to 180° C. The treated oil is drawn off at *D* while the excess of hydrogen passes away at *B*.

In a supplement patent 221,890, of 1909, Erdmann recommends the steam distillation from the reaction chamber of the saturated product under diminished pressure.

Vereinigte Chemische Werke A. G.* make use of a palladium catalyzer precipitated on an indifferent body as a carrier and recommend as carriers finely-divided metals which do not have anti-catalytic properties, also metal oxides and carbonates. Under these circumstances it is stated that one part of palladium is sufficient to convert in a few hours 100,000 parts of oily material to a firm mass. They recommend the use of a hydrogen pressure of two to three atmospheres and a temperature somewhat above the solidification point of the saturated fat. They caution against arsenic, hydrogen phosphide

* German Patent 236,488, Aug. 6, 1910; also British Patent 18,642, 1911.

and sulfide, liquid hydrocarbons and carbon bisulfide, chloroform, acetone and free mineral acids as being destructive to the activity of the catalyzer.

Kayser * describes a process of treating oil with metallic catalyzer consisting in mechanically agitating the oil and catalyzer in the presence of hydrogen, preferably under pressure. One form of the apparatus indicated by Kayser for this purpose is diagrammatically represented by Fig. 11.

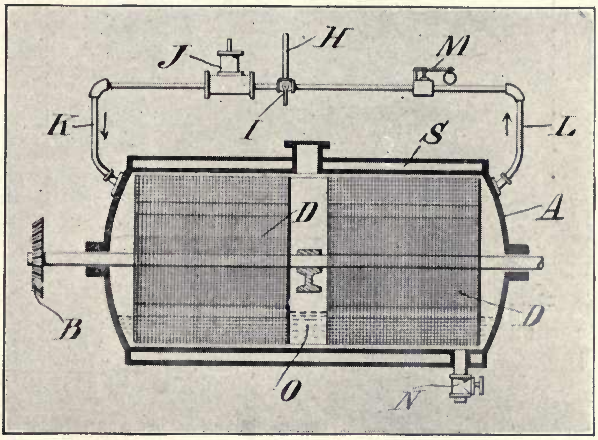


Fig. 11.

Here A is a closed horizontal cylindrical vessel in which is a paddle wheel D, made up of blades carrying wire gauze. The paddle wheel is rotated by a driving gear at B. In the upper part of the tank is an inlet for charging oil and presumably also the catalyzer, the oil being admitted to the tank in an amount sufficient to fill to perhaps one-fourth or one-fifth the entire capacity. Hydrogen is admitted at H and passes, by the three-way cock I, to the compression pump J, going from there to the treating receptacle. At the opposite end of the tank is an exhaust pipe L, carrying a blow-off valve M, for the purpose of venting the unabsorbed hydrogen. The temperature of treatment is stated to be about 150° to 160° C. Although the claims call for the use of hydrogen under pressure, no working pressures are specified. Fig. 12 shows diagrammatically one form of construction of the screen-covered paddle wheel used by Kayser.

In another U. S. Patent 1,008,474, of Nov. 14, 1911, Kayser sets

* U. S. Patent 1,004,035, Sept. 26, 1911.

forth the use of an inert pulverulent material such as kieselguhr as a carrier for the nickel catalyzer, he apparently having determined, as did Sabatier and others, that in some cases hydrogenation is more rapid

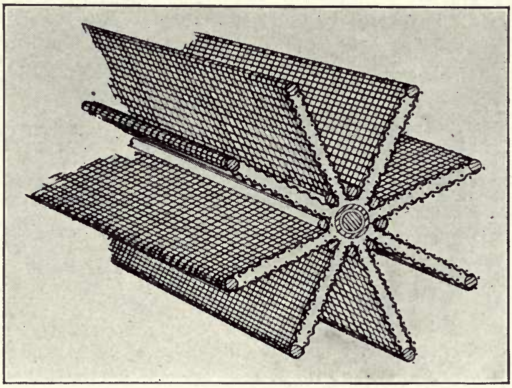


Fig. 12.

or complete when a carrier for the catalyzer is used; and he claims the process of hydrogenating oil involving agitation of a metal-impregnated inert pulverulent carrier (kieselguhr) with a fatty oil in the presence of hydrogen. It is commonly understood that the Kayser process is in operation on a large scale in this country.*

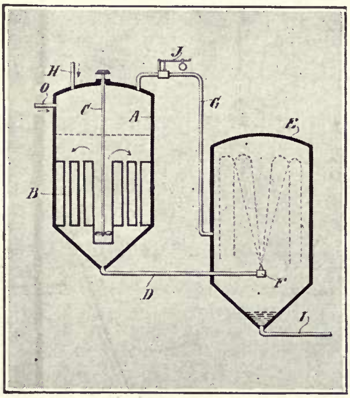


Fig. 13.

Two patents relating to the spraying of oil into a chamber containing compressed hydrogen have attracted some attention abroad. One of these is British Patent 7726, of 1910, to **Testrup,** and the other is to **Wilbuschewitch** which finds its counterpart here in U. S. Patent 1,024,758, of April 30, 1912. Fig. 13 shows the elements of the Testrup process.

Oil and catalyzer are pumped through the pipe *O* into the tank *A*, and hydrogen is admitted by the pipe *H* to furnish a gas pressure of, say, 15 atmospheres. The tubes *B* are

* The Kayser patents are assigned to the Proctor and Gamble Co., which concern is a large producer of hardened oil. A product termed "Crisco" is used as a substitute for lard.

heated by steam and the stirrer *C* circulates the oil and catalyzer in the tank *A*, until the oil has become heated and presumably somewhat hydrogenated. The oil is allowed to pass into the adjacent tank *E*, entering this tank by the spray nozzle *F*. Hydrogen gas is admitted to the tank *E* from the tank *A*, so as to afford a pressure of, say, 12 atmospheres in the tank *E*. A series of tanks may be arranged with a constantly decreasing pressure so that the differential pressure enables the spraying of the oil from tank to tank. Testrup states that spraying the material ten or fifteen times is sufficient to bring an oil of an iodine number of 110 down to an iodine number of 50.

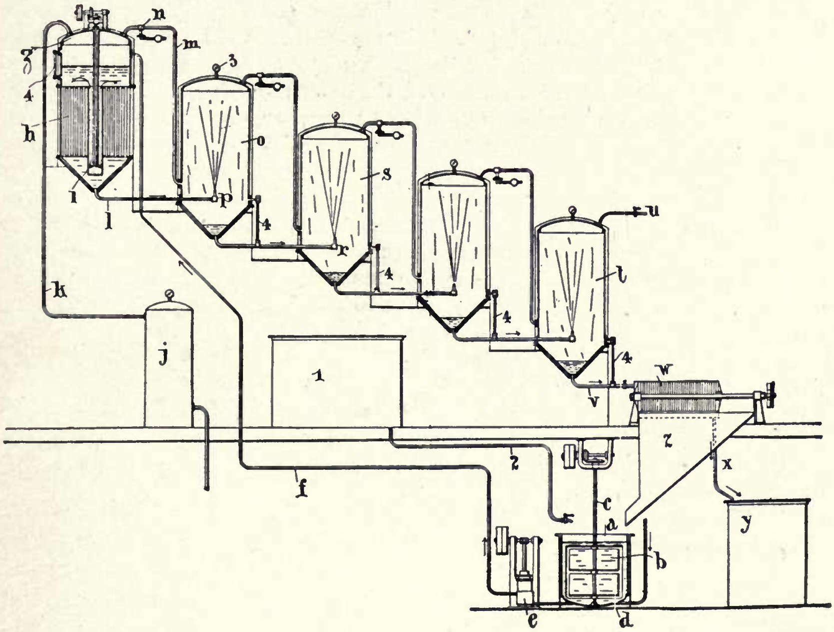


Fig. 14.

According to one form employing the apparatus shown in Fig. 14, and treating cottonseed oil, the oil, mixed with a suitable contact substance, such as finely-divided palladium or preferably nickel, is placed in a vessel *a* provided with a stirring device *b* comprising blades or like elements fixed to a vertical and rotatable shaft *c* within it. The amount of nickel may be about 2 to 3 per cent by weight. This vessel is preferably jacketed as at *d*, and is heated by the passage of heated fluid through this jacket, say to about 160° C. From this chamber the oil is pumped by a pump *e* through a conduit *f* and enters a vessel *g*, which is jacketed and heated by tubes *h*, being also provided with a mixing device comprising a central tube and propeller arrangement *i*. Hydrogen gas is supplied at high pressure from a reservoir *j* through

a duct *k*. The vessel *g* has an educt *l* for the material under treatment at its base and an educt for hydrogen *m* provided with a loaded valve *n*. The duct *m* opens into a vessel *o* into which the oil from the vessel *g* is sprayed by a spray nozzle *p* attached to the end of the duct *l* by the pressure of the gas in the vessel *g*. The oil and catalyst thus exposed to the action of the gas fall into the base of the vessel *o* to be forced by the pressure of the gas therein through a duct to a nozzle *r* in another vessel *s* wherein the operation is repeated. Several such vessels are arranged in this way in cascade, all being jacketed to allow of maintaining the desired temperature. The last vessel *t* is provided with any suitable educt *u* for the gas and an educt *v* for the treated oil and catalyst which is passed to a filter press *w* in which the oil is separated from the catalyst, the former passing by a duct *x* to a reservoir *y* and the catalyst being returned to the vessel *a* for which purpose the chute *z* may be utilized. Should the catalyst have become contaminated with nickel soap it may be purified as by washing with acid. A storage tank for the material awaiting treatment is indicated at 1 with its duct 2 leading to the vessel *a*. Gauges for noting the pressure 3 and the level gauges 4 are also employed. The temperature at which the reaction is conducted is about 160° to 170° C., and the pressure of the hydrogen in *g* may be about 15 atmospheres, in *o* say 12 atmospheres, the difference in pressure producing the spray. The pressure may similarly fall by 3 atmospheres for each vessel. It may be necessary to pass the substance again through the apparatus or to provide several systems of heaters and spraying devices in series in order to obtain the desired result but by this process the desired number of repetitions can be carried out rapidly.*

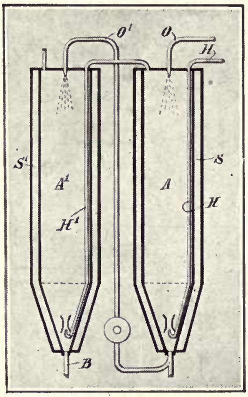


FIG. 15.

Even such a number of treatments are stated to require only about 30 minutes or less and the number of treatments would depend largely on the activity of the catalyst employed.

The **Wilbuschewitch** Patent itself details a rather complicated system, and Fig. 15 shows only what appears to be the essential features of the treating apparatus. Several tanks or autoclaves are connected as shown at *A* and *A'*, oil entering the top of the tank *A* by the pipe *O*, to form a spray which in descending meets an upward current of hydrogen entering by the pipe *H*. The oil is drawn off through the pipe *O'*, and sprayed into the tank *A'*. This time it meets a current of hydrogen represented by the excess of hydrogen coming from the tank *A*. The treated oil is drawn off and may be centrifuged to remove the catalyzer. A pressure of nine atmospheres is recommended and the pressures may be varied in the different tanks.

* Swedish Patent 992, May 27, 1911 (Techno Chemical Laboratories, Ltd.), on the hydrogenation of organic substances involving a process which essentially consists in mixing catalyzer with the substance to be treated and in subjecting the mixture in an atomized or finely-divided condition to the action of hydrogen, leads

Of the Wilbuschewitch process **Goldschmidt** * states that the high hydrogen pressures employed enable the reaction to take place quickly at temperatures between 100° and 160° C., so that the fat is not likely to be injured by the temperature to which it is subjected. It should be stated that several years previous to the date of the Wilbuschewitch patent, Ipatiew had noted and carefully studied the action of increased pressure.

Bedford and **Williams** have brought out an interesting process represented by U. S. Patent 1,026,339, of May 14, 1912. Fig. 16 shows the apparatus indicated by Bedford and Williams for carrying out the process. Oil is placed in the receptacle *A*, which is heated by

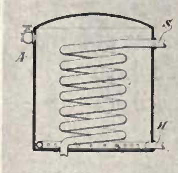


FIG. 16.

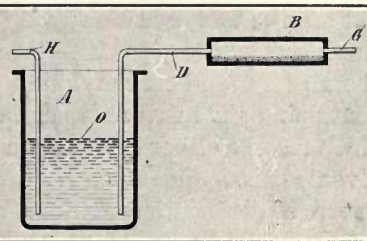


FIG. 17.

a steam coil *S*. Metallic *oxide* catalyzer is added, about 1 per cent being recommended, and hydrogen and oxygen or air is introduced by the pipe *H*. As a catalyzer, nickel oxide † is recommended and instead of the customary hydrogenating temperatures of 150° to 170° C., a temperature of about 250° C. is employed. While hydrogen alone may be used for the purpose, the inventors recommend and claim treatment of the oil with a mixture of hydrogen and oxygen to form hydroxy fatty acids or their glycerides.

A process for the conversion of fatty acids or their glycerides into saturated bodies in which a finely-divided metal oxide serves as a catalyzer is described by Bedford, Williams and Erdmann, ‡ and the reaction is carried out under pressures ranging from atmospheric pressure up to but not exceeding 20 atmospheres. Nickel oxide is especially recommended as the catalytic material.

the editor of Chemiker Zeitung (Chem. Zeit. Rep. (1913), 320) to make the comment that it is somewhat questionable according to other investigations which have been made in this direction, whether this process is practical for the manufacture of edible fats and the like.

* Chem. Ztg., 1912, 945.

† Previously used by Ipatiew.

‡ Siefen. Ztg., 1913, 1413.

Shukoff * claims the process of hydrogenating oils by means of nickel derived from the decomposition of nickel carbonyl. The carbonyl may be obtained from reduced metallic nickel by passing carbon monoxide over it at a low temperature. Nickel carbonyl is soluble in oil and is very readily taken up by gases. On heating to a temperature of 200 degrees or so, the carbonyl is decomposed, setting free, in a nascent state, metallic nickel which acts as a catalyzer. Shukoff makes use of this reaction of nickel carbonyl by the method indicated by Fig. 17. Carbon monoxide is passed by the pipe *G* into the tube *B*, containing finely-divided nickel and the nickel carbonyl formed is conducted to the oil *O*, which is heated to about 180 degrees. After sufficient nickel catalyzer has formed in the oil, the carbon monoxide stream is cut off, the temperature raised to 220° or 240° C. and hydrogen gas introduced by the pipe *H* to bring about hydrogenation.

Schukoff states if nickel carbonyl in a gaseous condition or a nickel-carbonyl-containing gas mixture is conducted into the material to be reduced, which may be either in a molten condition or in solution in a suitable solvent, it is found, when the temperature advances beyond the temperature of dissociation of nickel carbonyl, that metallic nickel in an extremely finely-divided state is separated and that the division obtained in this way is so fine as to cause the reaction mixture to appear black in color, and the separated nickel settles only after very long standing. As an example: Into 8 kilos of cottonseed oil warmed to 180° C. a slow stream of 400 liters of carbon monoxide is passed, which carbon monoxide has previously passed over a long layer of metallic nickel warmed to about 60° C.; finely-divided active nickel separates in the oil; the stream of carbon monoxide is then interrupted, the temperature raised to 230° to 240° C., and hydrogen as a slow stream is run into the mixture during a period of five to six hours in an amount of 3000 liters. The reaction mixture on cooling is completely hard; by filtration the nickel can be removed and the product eventually converted into stearic acid.

Day has taken out U. S. Patent 1,004,632, of Oct. 3, 1911, supplementing his earlier patent on the treatment of hydrocarbon oils with hydrogen. In the present instance tubes packed with catalyzer are placed in an oil still in such a manner that vapors from the oil may pass through the catalyzer tube in conjunction with hydrogen while being superheated by exterior contact of the tubes with boiling oil.

An English Patent, 23,997, of 1909, to **Phillips** and **Bulteel** claims

* German Patent 241,823, Jan. 18, 1910. See also H. Kamps, Belgian Patent 246,975; Seifen. Ztg., 1912, 1339. U. S. Patents, 738,303, 777,848 and 943,627 are of incidental interest.

to convert mineral oils into oils of lower specific gravity by heating with hydrogen in the presence of nickel or other catalytic agents. They state that the mixture of oil, gas and catalyst may be blown into a heated cylinder and the jet given a gyratory motion either by means of a nozzle revolving about its axis or by injecting the mixture tangentially to the periphery. In the latter case they state that the cylinder may have an axial core.*

The firm of **H. Schlinck & Co.**, of Hamburg, Germany,† hydrogenate oil by passage through a centrifuge, the drum of which carries a porous lining supporting palladium catalyzer which offers a frictional resistance to the passage of the oil. Fig. 18 shows a centrifugal drum *a*, which is closed at the top and can be heated. Oil and hydrogen are introduced through the pipe *b*. Openings are provided in the walls of the drum in which is placed rough or porous material covered with precipitated palladium. Several drums may be arranged in series

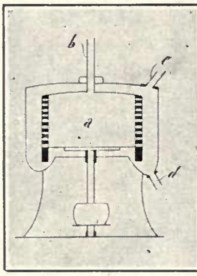


FIG. 18.

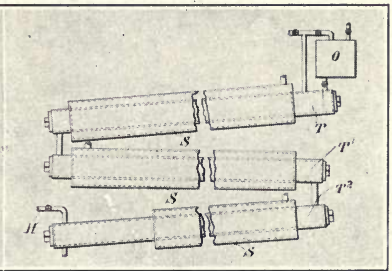


FIG. 19.

* In the treatment of hydrocarbons with superheated steam Hausmann and Pilat (German Patent 227,178, 1909) recommend as catalyzers the oxides of iron, lead, cerium and manganese, also iron sulfate and calcium manganite. Richter (German Patent 240,760, 1910) makes use of active carbon as a carrier for oxygen in the treatment of petroleum and other oils. Leffer (British Patent 2328, 1912) distils petroleum oil under pressure while circulating an inert gas through the body of oil in the still. Leffer mentions hydrogen among the inert gases suitable for the purpose. Lamplough (British Patent 19,702, 1912) proposes to effect reaction between petroleum oil and water by passing a mixture of the vapors of these bodies over rods of metallic nickel while subjecting the vapors to a pressure and to a temperature approaching a dull red heat. From 20 to 60 parts of water are used to 100 parts of oil. Dibdin and Woltereck (British Patent 19,152, 1901) bring a mixture of superheated steam and petroleum oil into contact with iron, copper and other metals maintained at a bright orange heat to effect the simultaneous decomposition of the steam and hydrocarbon. They also mention (British Patent 26,666, 1905) the use of "protoperoxide" of iron.

† British Patent 8147, 1911. The corresponding patent in the United States is 1,082,707, Dec. 30, 1913.

through which the oil may be caused to progress until sufficiently hydrogenated.

Ellis * uses a stationary catalyzer, filling tubes with the material in granular form and allowing oil to flow through the tubes while passing hydrogen in an opposite direction. Fig. 19 shows a three-section apparatus with the catalyzer tubes T, T^1 and T^2, heated by the jackets SS. Oil from tank O flows through the apparatus while hydrogen, admitted by the pipe H, passes through in an opposite direction. The arrangement permits of differential heating so that, for example, the oil may be heated to a temperature corresponding to its particular degree of hydrogenation at any given point, enabling a hydrogenated product free from "burnt" odor to be obtained. Fig. 20 shows a vertical form of apparatus, the catalyzer being shown at C in the tube A.

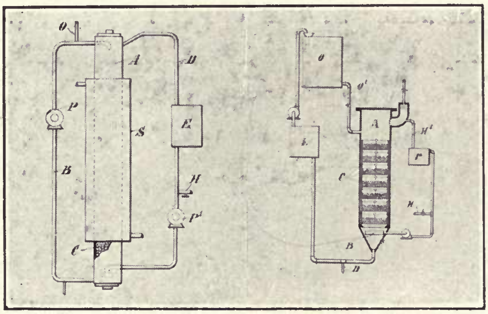


FIG. 20. FIG. 21.

Oil is introduced by the pipe O, and passes into the tube or cylinder A. The pump P causes oil to circulate from the top to the bottom of the apparatus through the pipe B. Hydrogen gas admitted at H is pumped into the bottom of the cylinder A, and the excess is withdrawn at the top by the pipe D, passing through the drier E, and back into the treating cylinder. Oil may be continuously fed through the pipe O in the upper part and the treated product withdrawn at the same rate at the lower part of the apparatus.

In another form † of the apparatus, the catalyzer is placed in trays or baskets as shown by Fig. 21 at C. The oil travels in a cyclic path downward through several layers of catalyzer, and hydrogen gas passes in an opposite direction. Separation of the catalyzer in layers in this manner enables the hydrogen to pass more uniformly through the

* U. S. Patent 1,026,156, May 14, 1912. See also U. S. Patent 1,052,469, Feb. 11, 1913.

† U. S. Patent 1,040,531, Oct. 8, 1912.

catalyzer bed. If the catalyzer forms a bed of considerable depth and width, the gas in taking the path of least resistance is liable not to come in contact with some parts of the bed.

The activity of a properly made catalyzer is oftentimes surprising. In the case of a stationary catalyzer the author has noted instances of hydrogenation where oil is converted into a hardened fat by scarcely more than momentary contact with the catalyzer.

Fig. 22 shows a photograph of a small laboratory apparatus for testing catalyzers, consisting of an inclined tube containing the catalyzer and carried in a heating jacket. Oil is admitted at the right and hydrogen at the left-hand end. Fig. 23 shows the catalyzer tube at the right from which extends a horizontal tube supplying hydrogen to the catalyzer tube.

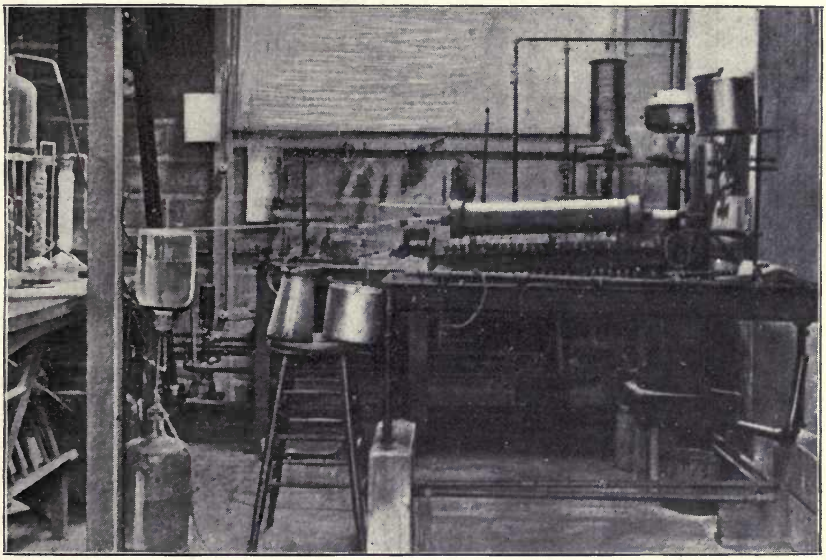


Fig. 22.

When using a new type of catalyzer the author started to pass oil through the catalyzer tube and found hydrogen to be absorbed so vigorously by the oil that instead of passing off through an oil seal at the lower end of the inclined catalyzer tube, the oil, curiously enough, was impelled against the strong current of hydrogen passing through the horizontal tube, rushing through it to the point indicated by the hand of the operator (Fig. 23) and there solidifying, actually being well hydrogenated from its brief passage through the apparatus. A

peculiar feature was the advance of the oil from the tube containing catalyzer far into the tube through which only the hydrogen was entering the apparatus. The travel of the oil along the hydrogen-supplying pipe in opposition to a rapid current of hydrogen indicates the possibility of hydrogenating in a very short time, provided a catalyzer of a high degree of activity is secured.

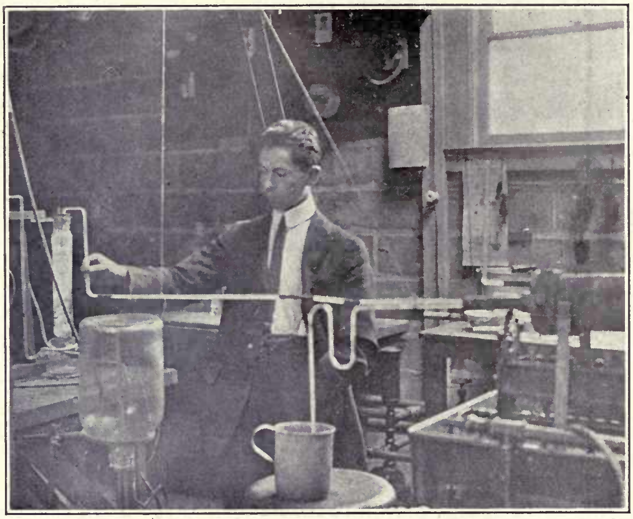


FIG. 23.

On the other hand, some catalyzers of the nickel and cobalt type when first brought into contact with oil and hydrogen show for a time a certain degree of sluggishness, but after a period, their activity rather suddenly augments and thenceforth remains apparent for a long period. This sluggishness should not be confounded with the seeming initial inactivity in the hydrogenation of oils containing considerable linolein or other highly unsaturated bodies. In such cases the rate of " hardening " (increase in melting point) is slow at first and later progresses more rapidly. Hydrogenation, in some cases at least, apparently proceeds selectively with initial formation of olein from linolein. Later the olein is transformed into stearin with the observed more rapid increase of titer.*

* Mailhe (Rev. gen. des Sciences, 1913, 653) makes note that he has seen cottonseed oil hardened to a high titer by twenty minutes exposure to hydrogen and catalytic material.

Marcusson and *Meyerheim* * have reached the conclusion that fish oil (tran) does not hydrogenate selectively or by stages, that is to say, the more highly unsaturated components do not largely take up hydrogen before olein becomes converted into stearin. A certain percentage of the highly unsaturated fatty acids remain even after a large proportion of the oleic acid has been transformed into stearic acid. The inner iodine number (iodine number of the liquid fatty acids) of a sample of hardened tran was found to be 107, which result led to the foregoing conclusion.

Ellis † effects a constant circulation and contact of the hydrogen gas in accordance with the method shown by Fig. 24. The tank *A* contains a body oil *O*, the space above the oil being filled with hydrogen under any suitable pressure. The tank is heated by the jacket *S*. A pump *P* withdraws the hydrogen from the upper part of the tank and impels it through the pipe *D* into the lower part of the tank. The catalyzer is added to the oil when the proper temperature is reached and the constant bubbling of a stream of hydrogen through the oil causes intimate contact between the reacting elements. After the

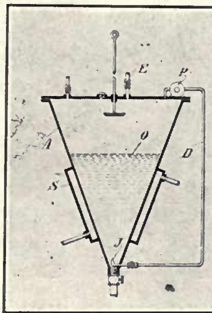


FIG. 24.

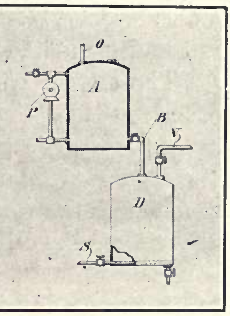


FIG. 25.

operation is completed, the porous plate, fastened to a movable stem in the upper part of the tank, may be depressed to fit into the bottom of the conical base so that when the oil is withdrawn a good portion of the catalyzer remains without exposure to the air and may be used with perhaps a small addition of fresh catalyzer for the treatment of a succeeding charge of oil.

In U. S. Patent 1,043,912, Ellis hydrogenates oil (Fig. 25) in the autoclave *A*. The pump *P* circulates hydrogen gas through the oil. The treated product is run into the deodorizer *D*, where it is treated

* Zeitsch. f. angew. Chem. 1914, No. 28, 201.
† U. S. Patent 1,059,720, April 22, 1913.

with superheated steam under diminished atmospheric pressure until the oil is freed from noxious gases or vapors. While the deodorization of ordinary cottonseed oil, for example, requires a temperature from 200° to 300° C. and a vacuum of down to one or two inches mercury, the deodorization of the hydrogenated cottonseed oil does not necessarily require as high a temperature and the vacuum " pulled " may be considerably less.

Contrary to the opinion entertained by many it does not appear needful to violently agitate the catalyzer primarily for the purpose of contacting it with hydrogen. Once the catalyzer is wetted with the oil there can no longer be any actual contact with the gas. Hydrogen reaches the catalyzer seemingly only through solution in the oil. The forces of adhesion effectually seal the catalyzer surface from the gas, and no measure of agitation by ordinary mixing apparatus will dislodge the film of oil. Of course, agitation secures the rapid replacement of more saturated by less saturated portions of the oil, but this replacement, under certain conditions, may proceed rapidly, simply by diffusion.

The direct pumping of hot hydrogen gas, especially if the latter is under considerable pressure, offers some difficulties, and the apparatus shown in Fig. 26 is designed to effect a circulation of the gas by inductive effect.* The tank 1 carries an inductor 2 through which is forced oil propelled by the pump 3. The passage of the oil through the inductor causes hydrogen, which is supplied to the upper part of the tank, to be drawn into the central vertical pipe and carried with the oil to the bottom of the tank when the gas bubbles through the main body of oil. Thus the oil which is being treated is made use of to circulate the gas.

Another type of apparatus † involves circulating hydrogen gas by means of an oil sealed pump which may be so arranged as to permit the return of any hydrogen escaping through the stuffing boxes. Fig. 27 shows this apparatus. 1 is an oil treating tank with gas outlet 2, communicating with a drier or purifier 3. From the lower part of the latter a pipe leads to the pump 4 which is enclosed by the housing 5, the space between pump and housing being filled with oil. The pump discharges into the lower part of the tank through the gas distributor 6. A connection 7 from the upper part of the housing to the tank provides a vent for gas escaping from the pump.

In hydrogenating oleic acid in a vaporized state **Shaw** ‡ obtained

* U. S. Patent to Ellis, 1,059,720, April 22, 1913.
† U. S. Patent to Ellis, 1,071,221, Aug. 26, 1913.
‡ Seifen. Ztg., 1912, 713.

some rather curious results. As a hydrogenating apparatus Shaw used a glass tower, holding catalyzer, the latter being prepared by putting fragments of pumice into a 50 per cent solution of nickel nitrate. The pumice was heated to a red heat in order to convert the nitrate to the oxide and the process repeated in order to get a good coating. The material was then placed in the glass tower and reduced by hydrogen at about 300° C., reduction taking place in 2 to 3 hours. The tower was heated in an oil bath.

Oleic acid was supplied from a distilling flask which was connected with the tower by gas-tight piping. In the flask was inserted a tube through which hydrogen could be introduced. The hydrogen was generated in a Kipp apparatus, passed through wash bottles containing nitric acid and sulfuric acid, and finally through a "U" tube containing fragments of caustic potash. From the tower a delivery tube extended to a receiver which was connected with a manometer and an air pump. The temperature of the oleic acid was maintained a few degrees above the boiling point of the acid, or about 300° C. In this way the catalyzer was never wetted with the liquid acid, but came in contact only with the gaseous acid which distilled over from the flask. The reaction product was condensed in the receiver.

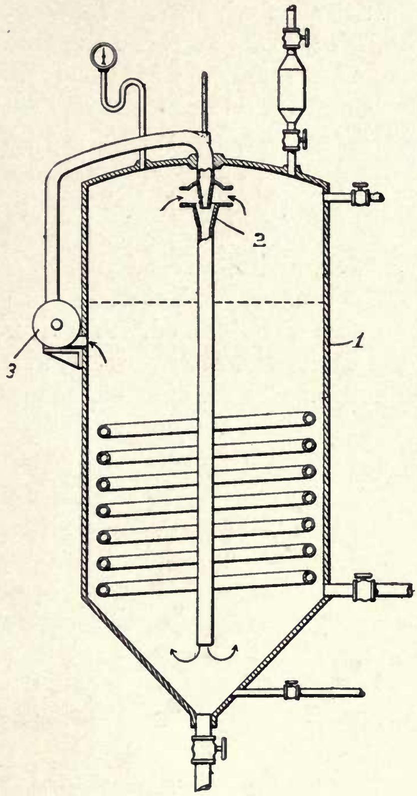


FIG. 26.

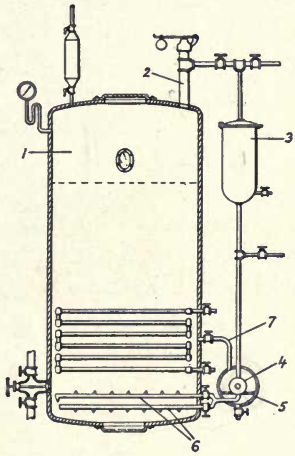


FIG. 27.

The degree of reduction was determined through the iodine number with the following results: the iodine number of oleic acid employed was 79. When distilled under a pressure of 100 mm., the resulting product had an iodine number of 75, which corresponds to a reduction of 5 per cent. This partially reduced product under a pressure of 100 mm. was distilled through the catalyzer, and the product obtained had an iodine number of 74.8, practically identical with the previous value. In reviewing this unfavorable result it was concluded that the catalyzer was poisoned and its activity lost. To test this out a fresh portion of oleic acid was distilled through the catalyzer. Again a reduction of 5 per cent occurred, which indicated that the catalyzer was not poisoned.

Distillation at 150 mm. was then tried, giving a reaction product having an iodine number of 68 to 70. When this product was distilled again at 150 mm., the same iodine number was obtained. A pressure of 200 mm. was then employed and the reduction was 20 per cent, while a second distillation at 200 mm. did not increase the amount reduced.

These results suggested the possibility of an equilibrium between stearic acid, oleic acid and hydrogen, and that the reduction degree which Shaw found varied from pressure to pressure was constant for any one pressure. If this conclusion were correct, then the equilibrium should be reached from the opposite end, namely through distilling stearic acid in the presence of hydrogen. In order to see whether this were possible stearic acid was treated in exactly the same way as the oleic acid by distilling through freshly prepared catalyzer. As a result of the test it appeared that stearic acid experienced no change in iodine number which apparently excluded the idea that conditions of equilibrium were involved.

Shaw's observations that by repeated distillation of oleic acid no further reduction occurs was not to be explained on the ground of fractional distillation of the partially reduced product, for the entire contents of the flask were distilled through the catalyzer, and furthermore the boiling point of stearic acid differs very little from oleic acid, so Shaw is at a loss to explain the cause of this peculiar behavior after finding it not due either to the existence of equilibrium or fractional distillation.

An investigation was made to determine what influence length of time had on the progress of reduction. The same apparatus was used. Oleic acid was distilled under diminished pressure and the temperature of the oil bath maintained at 275 degrees, while small quantities of the acid were distilled over in definite time intervals and the iodine number determined.

The following is the result:

2 hours	Iodine No. 67	M. P. 23°
3½ hours	Iodine No. 62	M. P. 33°
5 hours	Iodine No. 60	M. P. 37°
9 hours	Iodine No. 45	M. P. 50°

Shaw also determined the effect of pressure considerably above atmospheric and found:

With pressure of 5 atmos.;	temp. 250° C.;	Iodine No. 77
With pressure of 25 atmos.;	temp. 250° C.;	Iodine No. 64
With pressure of 50 atmos.;	temp. 250° C.;	Iodine No. 52

by which he concludes that the reduction progresses in proportion to the increase in pressure.*

In the decomposition of fats, oils and waxes into fatty acids and alcohols by aromatic sulfonated fatty acids, the fats or fatty acids used in preparing the latter, according to **Connstein** and **von Schonthan,** are reduced before sulfonation, either by catalytic processes or by electrolysis.† For example, castor oil is hardened by treatment with hydrogen, using palladium catalyzer; equal parts of the hardened product and naphthalene are mixed and to the mixture twice its weight of sulfuric acid of 66° Baumé is added, avoiding an increase of temperature above 20° C.

The reaction mixture is stirred until homogeneous and is then poured into somewhat more than its own weight of water. The oily layer which separates is filtered and is then ready for use. An illustrative example of the process by the patentees calls for treatment of 1000 parts of palm kernel oil, 300 parts of water and 2 parts of the fat cleavage compound for 6 to 8 hours with dry steam. After separation of the two layers the lower layer or glycerine water is concentrated in the customary manner while the upper layer consists of fatty acids.

According to **Steffan** ‡ this fatty cleavage reagent has been placed on the market under the name of "**Pfeilring.**" § Steffan comments on the discoloring action of the Twitchell process on some fats and oils among which he mentions certain grades of tallow, soya bean oil and fish oil, the coloration of whose fatty acids when produced by the

* Sabatier notes in his book on Catalysis, Paris, 1913, 78, that the vapors of oleic acid entrained by a strong current of hydrogen and passed over nickel heated to 280° to 300° C. are rapidly transformed into stearic acid, and the same thing occurs with the isomer elaidic acid. (See Ann. Chim. Phys. (8), 16, 73, 1909.)

† British Patent 749, Jan. 10, 1912, Vereinigte Chem. Akt. Ges.

‡ Seifen. Ztg., 40, 550.

§ "Pfeilring" cleavage composition from the patent standpoint is critically discussed by Esch (Chem. Rev. u. d. Fett u. Harz Ind. (1913), 295).

Twitchell process being so dark that when made into soaps the color of the product leaves much to be desired.

Fat cleavage reagent prepared with the hardened oil is claimed to produce a much lighter fatty acid. The rate of saponification with the hardened oil product Pfeilring is approximately that of the Twitchell reagent. Using equal parts of the two reagents under like conditions the following results were obtained:

	5 hours, per cent	23½ hours, per cent	34 hours, per cent
Twitchell reagent	37.23	83.31	88.94
Pfeilring reagent	36.92	80.18	88.69

These results indicate for Pfeilring a rate of cleavage slightly less than that of the Twitchell reagent, but it is brought forward by the supporters of Pfeilring that, the latter reagent being in itself very light colored, while the Twitchell reagent has a blackish cast, the proportion of the latter which may be used is limited by the required color of the resulting fatty acids, but that Pfeilring may be used in larger proportion without the danger of discoloration and hence the rate of cleavage may be increased by using a larger quantity of the reagent while the reaction may be carried more nearly to completion, that is to 95 per cent and over, without the discoloration sometimes observed in the Twitchell process.

In response to a critical discussion of the properties of soaps made with hardened oils * **Sudfeldt Brothers** state † that for several years they have been splitting large quantities of hardened whale oil by the Twitchell process and converting the fatty acids into soap and have found these fatty acids to be of good color and the soaps prepared from them to be in no wise lacking in color. The sharp odor noticed in the neutral fat is not lost by the splitting operation and also appears in the finished soap.‡

Reference has been made to the work of **DeHemptinne** on the effect of electrical discharge in causing the addition of hydrogen to unsaturated oils. Later work by this investigator § furnishes additional data on this interesting reaction. The formation of stearin by the action of an electric discharge on commercial olein in an atmosphere of hydrogen was studied on both a small and large scale. The apparatus employed on a large scale consists of a rotatable horizontal axle

* Seifen. Ztg. No. 25, 1912.

† Seifen. Ztg. (1912), 720.

‡ Sudfeldt & Co. contend in favor of the Twitchell reagent; Seifen. Ztg. (1913), 613. See also Seifen. Ztg. (1914), 311, 338 and 392.

§ Bull. Soc. Chim. belg., 26, 55.

bearing a large number of thin, parallel, vertical iron plates separated by glass plates, the former being connected together alternately on opposite sides. The whole is mounted in an air-tight iron drum which is partially filled with olein and into which hydrogen is introduced; the odd numbers of the iron plates are connected with one pole of a high-potential alternator and the even numbers with the other pole. When the axle is rotated, the electric discharge passes through a thin layer of olein which constantly wets the plates. The glass dielectric may be arranged so as to contact with one or both faces of the iron plates (the free space in the latter case being between the dielectrics) or the dielectrics may be separated from both faces of the iron plates. The capacity of the largest apparatus constructed was about 1000 pounds. Apart from the construction of the apparatus the yield is influenced by the current density, the frequency of the current, gaseous pressure, temperature of the liquid and the distance between consecutive iron plates. If the reduction is not pushed beyond a point corresponding to a 15 per cent decrease in the iodine number, there is a complete parallelism between the decrease in the iodine number, increase of melting point and absorption of hydrogen. The variation of the iodine number or the increase of the melting point per unit of electrical energy employed is taken as a measure of the transformation effected. A proportionality between the quantity of substance transformed and the intensity of current does not always exist. For a given intensity of current the quantity transformed reaches a maximum for a definite distance of electrical discharge; this maximum varies with the pressure. In order to obtain a satisfactory reaction the current must act simultaneously on both liquid and gas. Prolonged action of the current causes polymerization and the reactions become quite complicated. The apparatus can be used for deodorizing fish oil, as the unsaturated compounds of this oil take up hydrogen under these conditions. Because of the gradual polymerization produced the method is suggested as applicable for thickening mineral oils or mixtures of mineral oils with animal or vegetable oils. Molecular weights as high as 2500, as determined by the ebullioscopic method, were obtained. The viscosity of these polymerized oils varies less with the temperature than does that of the pure mineral oils; the coefficient of friction of the former is also stated to be less.

Apparatus patented by Hemptinne * is of the following character: A series of parallel rotatable metal plates, with discs of insulating material between adjacent plates, is arranged within a fixed casing or within a vessel that rotates with the plates on a horizontal axis.

* British Patent 7101, April 4, 1905.

Alternate metal plates are connected to one pole, and the remainder to the other pole of a source of electric current, in order to establish a silent electric discharge between the plates. The latter are partially immersed in the absorbing liquid, which is carried around by small troughs attached to the casing and delivered on to the upper portions of the plates, so that a thin layer of liquid is maintained on the plates, and the gas to be treated is thus brought into intimate contact with the liquid. An electro-magnetic device, working automatically, maintains a constant pressure of gas in the apparatus during the absorption.*

A process for the production of neutral hydrogenated fats from raw material containing fatty acid involves hydrogenating the oil in the presence of glycerine under which condition the fatty acids are claimed to be converted into glycerides.†

With an apparatus as shown in Fig. 28, **Ellis** ‡ hydrogenates by passing a current of oil through a rotary drum containing catalytic

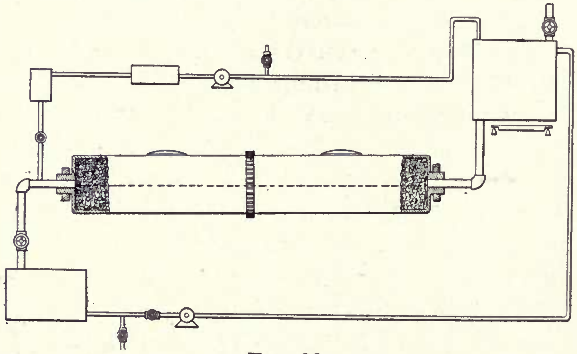


FIG. 28.

material supported on coarse fragments of pumice, so that on rotation of the drum the catalyzer moves in a direction substantially transversely to the direction of the oil current. Hydrogen may be passed through the drum as a counter-current. A given quantity of oil may be circulated in this manner until hardened to the requisite degree.§

* The application of the electric current in the industry of oils and fats has been reviewed by Buttlar (Chem. Rev. u. d. Fett und Harz Ind. (1912), 97) who discusses its use in the transformation of liquid oils into solid fats, also in the bleaching of oils.

† Seifen. Ztg. (1913), 263.

‡ U. S. Patent 1,052,469, Feb. 11, 1913.

§ In U. S. Letters Patent 1,095,144 of April 28, 1914, to Ellis a process is set forth for hardening oils which involves the movement of oil and catalyzer in a direction transverse to that of the hydrogen current.

CHAPTER II

METHODS OF HYDROGENATION — Continued

Utescher * treats oils with hydrogen in presence of a finely-divided catalytic agent, and at the same time the material is subjected to the action of a silent electric discharge.† In a description of the process, it is stated that the "silent discharge" is prevented from coming into actual contact with the fatty substance, only chemically active rays (e.g. from a mercury vapor lamp) being utilized. It is also stated that the process may be effected by allowing the rays to impinge on the surface of a catalytic substance, which may be used in the form of plates.‡

The joint application of a catalytic and an electric discharge is claimed to give a greater effect than either agent singly.§

Some observations on the effect of ultra-violet light on catalytic action have been made by **Farmer and Parker** ‖ which indicate that on colloidal platinum, at least, the ultra-violet light exerts a retarding influence on the rate of catalytic change. Colloidal platinum was prepared by the Bredig method, i.e., by producing an arc between platinum electrodes under distilled water. Hydrogen dioxide was used as a measure of catalytic activity. The colloidal platinum was exposed to the ultra-violet light and samples were drawn from time to time in order to get exposures of varying lengths, the samples being introduced into hydrogen peroxide placed in an apparatus shown in Fig. 29. The inclined tube of this apparatus was completely filled with dilute hydrogen peroxide solution and a bent delivery tube arranged to collect any liquid displaced. As colloidal platinum breaks

* British Patent 20,061, Sept. 3, 1912.

† Hydrogen activated by actinic rays is used for oil hardening (Seifen. Ztg. (1913), 1298).

‡ In this connection it is noted that the text of the Utescher specification of German Patent 266,662 of 1912 appears in Chem. Rev. u. d. Fett u. Harz Ind. (1913), 308.

§ Seifen. Ztg. (1913), 851. F. Gruner, French Patent 453,664, Jan. 27, 1913. Oils or fats are subjected to the action of a silent discharge of an electric current of very high tension and frequency. Currents of high potential (50,000 to 100,000 volts) and high frequency are employed.

‖ Jour. Am. Chem. Soc. (1913), 1524.

down hydrogen dioxide yielding oxygen, the evolution of the gas and consequent displacement of liquid enabled the rate of decomposition to be measured.

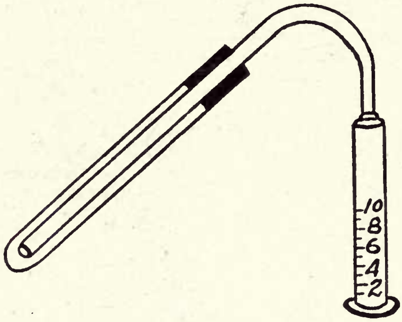


Fig. 29.

The experiments showed that the catalytic activity of the colloidal platinum was almost completely destroyed after an exposure of six hours, the activity then observed being no greater than that of the spontaneous decomposition of hydrogen peroxide itself. It was noted that the light caused the platinum to be precipitated out of solution as a black flocculent material. After such a precipitation it was in the form of large mossy clusters.

While no observations were made with respect to the hydrogenation of oils under these conditions, in view of the action of ultra-violet light on solutions of colloidal platinum, it would appear that exposure thereto may be expected to modify the rate of reaction in the hardening of oils.*

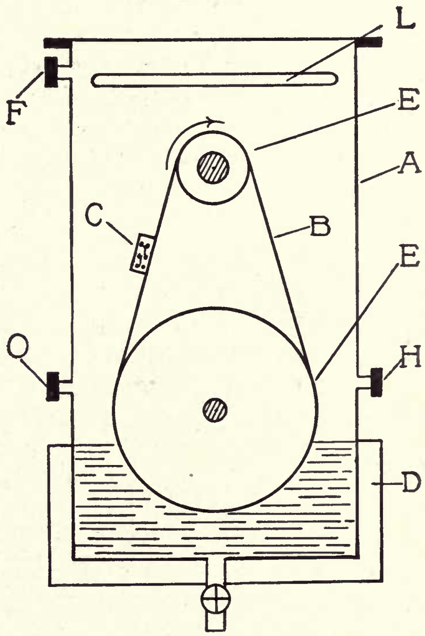


Fig. 30.

A process of hydrogenating oils involving exposure of the oil as a thin film on a web carrying catalytic material has been proposed by **Walter.**† Fig. 30 shows one form of apparatus described by Walter for carrying out this reaction. *A* is a closed vessel in which is placed a belt or web *B* carrying catalytic material. The belt may be made of asbestos or cotton cloth and may be impregnated with platinum, iridium,

* Some preliminary experiments by the author point to a reduction in the iodine number of cottonseed oil when exposed to ultra-violet light in an atmosphere of hydrogen.

† Seifen. Ztg. (1913), 442.

nickel or other catalytic material. The belt is carried on rollers *E*, one of which dips into the oil. Catalyzer also may be carried in the container *C* attached to the belt *B*. *D* is a steam or water bath. *H* is an inlet and *F* an outlet for hydrogen. *O* is an inlet for oil.

Two other types of apparatus are described: one consists of an upright stationary cylinder jacketed for about one-half the distance. The interior has a shaft with 4 arms upon which the catalyzer is carried and revolved through the liquid and gas. A bucket arrangement is also attached to the shaft to throw liquid upon the catalyzer. Another type consists of a jacketed horizontal cylinder with a rotating shaft supporting arms for carrying the catalyzer. (Figs. 31, 32 and 33.)

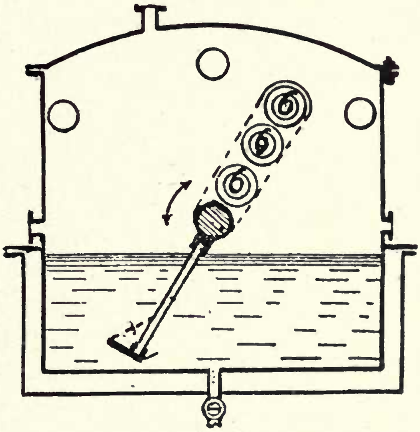


FIG. 31.

The operation may be carried out with the aid of chemically-active light for which purpose a lamp-lighting system of actinic character is shown at *L* positioned in the receptacle *A*. Walter lays great stress on the rapid absorption of hydrogen by oil or other material exposed in this manner in thin films. He states that although the film of oil on the belt covers the catalyzer, and in consequence one would expect the reaction to be hindered by the sealing effect of such a film, yet the liquid and gas react very quickly with one another. The solubility of the gas in the liquid, as well as the physical properties of the latter, he states, do not appear to play any essential part, for the sparingly soluble hydrogen exerts its reducing action apparently just as quickly in a thinly-fluid alcoholic quinine solution as it does in a viscous fish oil.

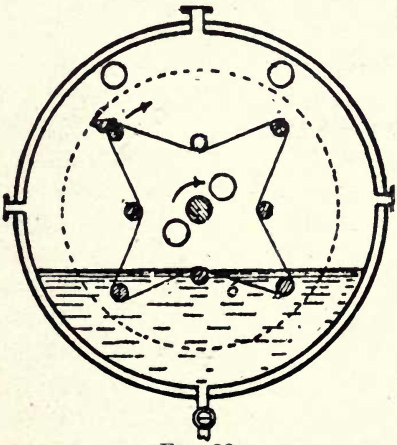


FIG. 32.

Walter recommends passing the oil through a series of receptacles

containing catalyzer attached to a belt as described or to an agitator arm, the arrangement being such that the oil first enters the receptacle which contains the weakest or more nearly spent catalyzer and after short treatment passes to the next container and so on until finally it reaches the last receptacle where the most active catalyzer is employed.

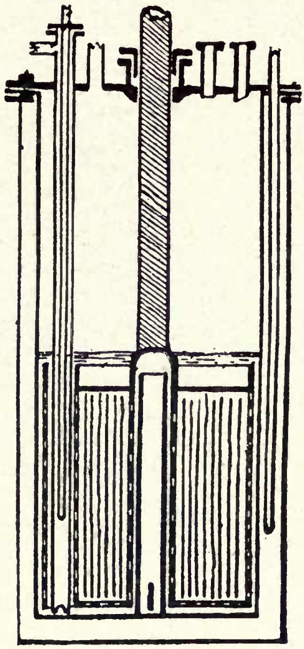


Fig. 33.

In connection with the above it may be stated that Walter has been granted German Patent 257,825, of July 27, 1911, which, in brief, has to do with the production of chemical reactions between liquids and gases under the influence of a contact substance or of chemically-active rays. Porous or roughened bodies, which may serve as contact substances, are supported on movable carriers and are caused alternately to dip into the liquid and then rise into the gas above the liquid, so as to bring fresh quantities of the liquid continually into contact with the gas, over a large surface. Several reaction chambers through which the gas and liquid pass in a definite order are preferably used. In some respects this resembles the process of Kayser previously discussed.

Birkeland and Devik * employ a form of apparatus which permits of forcing a mixture of oil and catalytic agent downwards through a nozzle into an atmosphere of hydrogen, filling the space above the bulk of the oil, which is contained in an autoclave. The hydrogen is drawn into the oil jets by injector action and subsequently rises in small bubbles through the body of oil. The process is preferably carried out under a pressure of 10 to 15 atmospheres and at a temperature of about 150° C. Sudden reduction of the pressure is claimed to promote the hydrogenation of the oil.

Brochet † treats unsaturated compounds as a class, by hydrogen, in the presence of a catalyst. Hydrogen or a gaseous mixture containing hydrogen is passed into the substance to be treated, either in the liquid form or in solution or suspension, in presence of a base-

* French Patent 456,632, April 14, 1913.
† French Patent 458,033, July 27, 1912.

metal catalyst, which may be held on an inert support. The velocity of the reaction is increased by working under pressure, although extremely high pressures are not necessary. By this procedure various unsaturated organic compounds may be made to combine with hydrogen.*

A somewhat elaborate gas-measuring system has been proposed by **deKadt.**† The amount of gas absorbed by a liquid or other material in a closed vessel, for example, in the combination of hydrogen with fats or oils in the presence of a catalyst, is determined by means of a gas meter or other measuring instrument arranged on the pipe supplying the gas and adapted to cut off the supply when a certain amount of gas has been supplied or combined. When apparatus is used in which the gas is introduced through a fine-spray nozzle at the bottom of the liquid, and unabsorbed gas from the top of the vessel is withdrawn and again introduced into the liquid, two meters are fitted upon the inlet and outlet pipes respectively so as to act differentially upon an indicator needle which thus records the difference between the volume of gas supplied and the volume unabsorbed. The needle may control an electric contact by which the gas supply is shut off and the circulating pump stopped as soon as the requisite amount of gas has been absorbed.

Fig. 34 shows the deKadt system.

The reaction vessel 1 is connected at its upper part through a suitable pipe connection 2 with a suction and force pump 3. At one part of its length this pipe connection 2 is formed into a cooling coil 4, which is located in a water reservoir 5. At the lower part of the reaction vessel 1 a nozzle or rose head 6 is provided, and from this nozzle a pipe 7 leads to the vessel 8 containing the hydrogen. This hydrogen-containing vessel communicates with the pump 3 by means of a pipe 9 and contains a cooling coil 12 provided with inlets and outlets for the supply and discharge of the cooling water.

The material to be treated, such as fats or oils, and the catalytically acting substances are supplied to the reaction vessel through a charging door 14. In the first place the hydrogen supply pipe 7 is cut off from the reaction vessel 1 and the pipe 9, connecting the hydrogen-containing vessel with the pump, is closed by a cock 15. The materials contained in the reaction vessel are then heated by means of a steam jacket or steam coil, and the air, contained in this vessel, is exhausted by means of the pump 3 and escapes to the atmosphere by way of the cock 16, the cocks 18 and 17 being open for this purpose. Hydrogen is then supplied through a pipe connected with the pump 3 and is forced into the hydrogen-containing vessel 8 through the pipe 9, the cocks 17 and 15 being open. When the necessary tension has been attained, the cocks 15 and 17 in the hydrogen supply pipe are closed and the cock 24 at the upper part of the reaction vessel connecting the vessel and pipe 2 are opened. A valve 19 is arranged in the pipe connecting the hydrogen vessel with

* See also First Addition dated Oct. 8, 1912.

† British Patent 5773, March 7, 1912.

the lower part of the reaction vessel by opening said valve 19, behind which a reducing valve 20 is arranged; the hydrogen is conducted by the pipe 7 into the vessel 1, where it passes from the nozzle 6 through the material to be treated with which it combines to some extent, while the excess escapes upwards and is again forced into the hydrogen-containing vessel 8 by the pump 3, the cocks being suitably adjusted. The supply of hydrogen contained in the vessel, which is not supplemented by a fresh external supply during the chemical reaction, must gradually decrease in tension owing to the combination with the contents of the reaction vessel. This decrease in tension can be utilized empirically for determining the progress of the chemical reaction or for ascertaining its various stages or its completion. These indications would, however, only be approximate and deKadt therefore provides means to interrupt the supply of hydrogen to the reaction vessel automatically after the consumption of the necessary quantity of combined hydrogen.

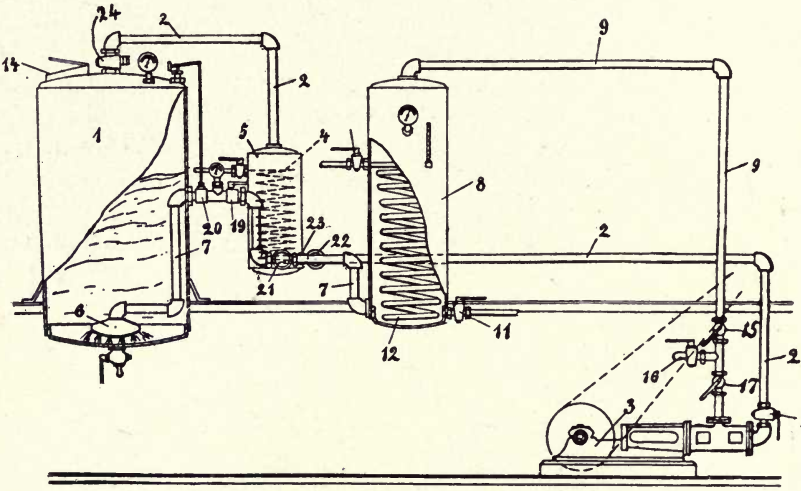


FIG. 34.

With this object a gas meter 21 is arranged on the pipe 7 supplying the hydrogen to the reaction vessel and indicates the quantity of hydrogen passing from the container 8 into the reaction vessel 1. A similar meter 22 is arranged on the return pipe 2 and measures the quantity of gas being withdrawn. Both these meters act on an indicating shaft 23 in such a manner that by the rotation of the shaft the first gas meter 21 moves the hand of indicating shaft 23 upwards, while the other gas meter 22 moves it rearwards so that the index hand shows the difference, that is to say the consumption of hydrogen. An electric contact is arranged in the path of the index hand and when it reaches a certain position, in which the necessary quantity of hydrogen has been consumed, the circuit is closed, and the hydrogen supply is cut off.

In hydrogenating oils containing the hydroxyl group, at high temperatures, this group is destroyed and **Markel** and **Crosfield** * propose

* British Patent 13,519, June 6, 1911.

the preparation of saturated hydroxy-fatty acids and their glycerides by treating the corresponding unsaturated acids or glycerides with hydrogen in the presence of a catalyst other than palladium and palladium hydroxide, at as low a temperature as possible, preferably just above the melting point of the final product, in order to avoid splitting off of the hydroxyl group or to control such splitting to any desired extent. Suitable catalysts recommended are iron, nickel, cobalt, copper, etc., also oxides, hydroxides and salts, which may be deposited upon suitable supports, preferably finely divided. As raw materials the mixture of unsaturated acids obtained by treatment of oleic acid with sulfuric acid, the oxidation products of linseed, cottonseed and rape oils, also castor, grape seed and whale oils may be used.

Temperature of Hydrogenation. For each compound there usually exists a well-defined range of temperature within which hydrogen is effectively added. Somewhere in this temperature interval lies the *mean effective temperature,* that is the temperature of maximum saturation velocity. For a number of fatty oils this approximates 180° C. or 356° F. with a nickel catalyzer. As a rule hydrogenation is accelerated more by a given temperature rise from below the mean effective temperature than the same temperature increase above this point retards the reaction. For example, raising the temperature from 170° to 180° C. increases the rate of hydrogen addition in a certain measure while elevating the temperature from 180° to 190° C. retards the rate, but to a lesser degree for such 10-degree temperature increment than the previous increase in the rate. In operation on the large scale it is, therefore, better to err by maintaining the oil slightly above rather than below the mean effective temperature, unless of course a lower temperature is prescribed because of the character of the oil. Rapidity of treatment often is desired especially in edible oils where protracted contact with the catalyzer introduces the danger of solution of the metallic material in the oil to an objectionable degree.*

The range of temperature mentioned above varies with each type of catalyzer. Platinum and palladium, at least in certain forms, may be used at temperatures between 80° and 100° C.; nickel between 160° to 200° C.; nickel oxide and copper at about 200° C. and upwards;

* The hydrogenation of unsaturated compounds, particularly fatty acids and their glycerides, into saturated compounds by hydrogen in the presence of finely-divided metal, according to Higgins is accelerated by the presence of formic acid or other volatile organic acid. The formic acid may be carried by the hydrogen, or the acid mixed with the material before treatment. (Chem. Abs. (1914), 437.)

all depending on the physical and chemical constitution of the catalytic material.*

Caro † considers the presence of carbon monoxide in hydrogen used for hardening fats with nickel catalyzers to be, under some circumstances, injurious to the catalyzer. Maintaining the temperature of the oil during hydrogenation above 200° C. is said to be beneficial as any nickel carbonyl formed will be at once decomposed at that temperature. The hydrogenation of many substances under these conditions is not feasible and Caro recommends that the gas first be passed over nickel at 180° C. to convert the carbon monoxide into methane, which is inert.

DeKadt ‡ saturates fatty acids or their esters with hydrogen by the use, as a catalyzer, of a soap of a heavy or noble metal, formed from a fat or fatty acids, whose melting point lies above that of the substance to be treated.§

It is claimed by **Fuchs** ‖ that his investigations have shown the present methods of reduction for the most part are improperly founded, causing long duration of time of treatment coupled with marked loss of hydrogen and heat; use of a great excess of hydrogen or catalyzer; injurious action of the long heating on the color, taste and odor of the reduced fat; and the application of high pressure in apparatus which involves costly autoclaves, dangerous to handle. Fuchs declares that the conduct of reduction of fatty bodies is essentially improved if the following theoretical conditions are observed:

(1) Thermal considerations: A quickening of the reaction is obtained when the oil to be treated is maintained at only a moderate temperature (0° to 150° C.), while the hydrogen employed is heated to 200° to 250° C. The avoidance of strong heating of the oil which is being treated is favorable to the quality of the final product, while preheating the hydrogen appears to increase its activity. Comparative tests show that in this way the speed of the reaction can be increased by about 10 per cent. For preheating the current of gas, copper or nickel coils in an oil bath are used. The oil bath may be

* Ipatiew (Chem. Ztg., 1914, 374) has noted that the hydrogenation of fatty acids with metallic nickel begins at 150° C. and with nickel oxide at 230° C. The reaction progresses readily at both high and low pressures.

† Seifen. Ztg. (1913), 852.

‡ Chem. Ztg. Rep. (1913), 541, British Patent 18,310, Aug. 9, 1912.

§ **Utescher** (Seifen. Ztg. (1912), 1044) discusses from the patent point of view the claims made by deKadt in Seifen. Ztg. (1912), 960; see also Seifen. Ztg. (1912), 900 and 1008.

‖ Seifen. Ztg. (1913), 982. Reduction of unsaturated fatty acids and their glycerides, Belgium Patent 256,574, 1913.

maintained at the requisite temperature through circulation of oil heated at a distant point.

(2) Chemical considerations: Since it is impossible to have free hydrogen in its most active form, that is, in a nascent state, act upon the oil to be treated, because the quality of the oil is injured, Fuchs observes that means must be provided to apply the hydrogen in the atomic form. This can be carried out through the application of chemically active rays. Dissociation of the hydrogen molecule appears also to occur when molecular hydrogen is passed over catalytic material such as palladium black or freshly prepared nickel powder and then is allowed to diffuse under high pressure through heated plates of metal. The activity of the dissociated hydrogen, it is claimed, is from 15 to 20 per cent higher than the normal gas. The catalytic material may be placed in a tube of suitable length or on the plates of a column apparatus. By way of illustration Fuchs states that cottonseed oil carrying 0.9 per cent of a catalyzer, prepared from nickel carbonate, is raised to a temperature of 120 degrees and is subjected to hydrogen under a pressure of 18 atmospheres, the gas having been chemically activated by passage through an iron tube 3 meters in length and 60 mm. in diameter, lined with platinized asbestos and heated to 250° C. In this way by two hours' treatment a fatty body having a melting point of 44° C. was prepared. In three hours a fat melting at 65.4° C. was obtained. Fuchs notes that ordinarily from 5 to 8 hours would be required to secure such products. The claims of Fuchs' Patent call for the reduction of unsaturated fatty acids and their glycerides by means of hydrogen according to the contact process, wherein strongly heated hydrogen is caused to react on only moderately heated oil; also the treatment of oil with atomic hydrogen whose activity has been increased by treatment with chemically active rays.

The employment of nickel carbonyl by Shukoff has been described in the foregoing. In a somewhat similar manner **Lessing** * makes use of a mixture of hydrogen and a gaseous metallic compound brought into contact with the substance under suitable conditions of temperature and pressure. Lessing states he has found that a great number of substances may be hydrogenated by treating them at elevated temperatures with hydrogen to which a metallic carbonyl vapor, or gas containing a metallic carbonyl, has previously been added; or with a mixture of gases, containing hydrogen in which metal carbonyl has been formed by combination of carbon monoxide, originally in the mixture, with a metal. The rapidity with which the hydrogena-

* British Patent 18,998, 1912.

tion proceeds under these conditions may be explained as the effect of the liberation of elementary metal, the properties of which "in statu nascendi" are known to be very different from those of metal which is merely finely subdivided. Lessing observes that it has already been proposed to use as the catalyzer finely-subdivided nickel, made by decomposing nickel carbonyl in the heated material prior to the introduction of the hydrogenating gas, but it was not known that technical advantages accrue from conveying the nickel carbonyl into the material simultaneously with the hydrogenating agent so that elementary liberation of nickel occurs in close contact with hydrogen and the substance to be hydrogenated. These advantages are that the proportion of catalyzer is very much reduced and the reaction proceeds much more rapidly. Lessing carries out his process in various ways. It is convenient to introduce nickel carbonyl into the hydrogen gas by passing a mixture of the latter with carbon monoxide over reduced nickel in the well-known manner for making nickel carbonyl.

The mixture of gases employed need not be of great purity and may be made from water-gas, or by the thermal decomposition of coal gas or of coke-oven gas or of hydrocarbons of any kind, but best results are obtained when the amount of carbon monoxide in the gases is limited to that requisite for forming the nickel carbonyl necessary for the reaction, and in any case the proportion of carbon monoxide in the mixture should not exceed 25 per cent. For example, when an oil such as a glyceride or a fatty acid is being hydrogenated, the simplest mode of operating consists in passing hydrogen containing 5 to 10 per cent of carbon monoxide first through a volatilizer charged with reduced nickel and then through the oil contained in a closed vessel heated to a suitable temperature, say from 200° to 240° C. The gases passing away from the vessel are returned to the volatilizer to be used again, hydrogen or a gas rich therein being added to compensate for that absorbed by the oil. The proportion of nickel required for the hydrogenation is very small; under proper conditions excellent results can be obtained with a proportion equivalent to 0.1 part of nickel to 100 parts of oil.

Another mode of operating consists in forcing the substance to be treated, if it is in a liquid form, through spraying nozzles into a gas-tight vessel which may be suitably heated to the temperature most favorable to the catalytic hydrogenation of the substance. Into the same container, preferably at or near the bottom, hydrogen gas containing metal carbonyl, for instance nickel carbonyl, is passed. The excess of gases leaves the vessel through an outlet at the upper part and may be returned into the gas circuit after the products carried with it have been separated by condensing or washing. The treated liquid may be drained off and returned to the reaction vessel until hydrogenation has proceeded far enough. Instead of heating the reaction vessel, or in addition to doing so, the liquid may be preheated in a suitable apparatus, before entering the vessel, to a temperature required for the reaction.

By another method of carrying out the process, a solution of metal carbonyl in oil is prepared, which may be accomplished by passing the gas carrying nickel car-

bonyl through cold oil. This solution is forced through a spray nozzle into a heated vessel where it meets hydrogen whereupon hydrogenation occurs.

If the compound to be treated is in the state of gas or vapor, as for instance in the hydrogenation of the more volatile tar oils, it is simply mixed with hydrogen containing the nickel carbonyl and is subjected to the temperature required for hydrogenation. Likewise in the case of a liquid some hydrogen may be mixed with the liquid, the spray being then preferably formed by injector action instead of by liquid pressure.

The use of nickel carbonyl for the production of catalytic material also has been patented by **Kamps,*** who introduces the carbonyl into an autoclave at a temperature above 43° C. and a pressure of 751 mm., and the oil which is to be reduced is maintained under such pressure and temperature conditions that the decomposition of the nickel carbonyl is brought about. At 60° C. the oil should be under a pressure of less than 2 atmospheres and at 180° C. less than 30 atmospheres.

Another method of utilizing nickel carbonyl for the production of catalytic material is that proposed by the **Bremen Besigheimer Ölfabriken** † according to which method kieselguhr or similar porous material is saturated with nickel carbonyl and the material is heated to cause the deposition of metallic nickel on the carrier. The nickel-containing powder is immediately ground with oil to form a paste-like mass, this operation being carried out with the exclusion of air. It is also stated that the contact material may be reworked in the following manner:

It is first purified by extraction, the nickel removed and after conversion of the latter into a pulverulent form is again used for the production of nickel carbonyl. It is recommended that the carbon monoxide obtained by the Linde-Caro process in the liquefaction of water gas be used for the production of the carbonyl.

A form of apparatus adapted to be used in carrying out a process of hydrogenating oils ‡ which relates more specifically to the treatment of rancid oils or oils of high acidity is shown in Fig. 35. An oil containing a high proportion of free fatty acids or products of rancidification may be diluted with a neutral oil and the mixture hydrogenated to a hard fat, although the original rancid oil be incapable of hydrogenation, because of its poisoning action on catalyzers. The apparatus consists of a tank having a dome in which atomizers are mounted and by which the oil is atomized with hydrogen gas, and is then allowed to trickle through a series of screens placed in the lower

* Belgium Patent 246,975.

† Zeit. f. angew. Chem. (1913), ref. 627.

‡ Ellis, U. S. Patent 1,078,136, Nov. 11, 1913.

part of the dome. Palm oil may be heated without access of air to a temperature at which its color is destroyed by hydrogenating under these conditions, producing a fat which is especially useful to soap makers.

A process for thickening oilsand fats is described by **Scherieble.*** The material to be treated is subjected to ozone-forming electric discharges by sending such discharges directly through it. Potentials of 10,000 to 20,000 volts yield no results, as oils and fats introduced between the electrodes impede any discharge by reason of their great insulating properties. Experiments in this direction have, however, shown that discharges through oils and fats are quite possible when high potentials of 50,000 to 100,000 volts and beyond are employed. The higher the potential of the electric current and the greater its frequency the easier it is to pass a discharge, with the formation of ozone, through thick layers of oil.

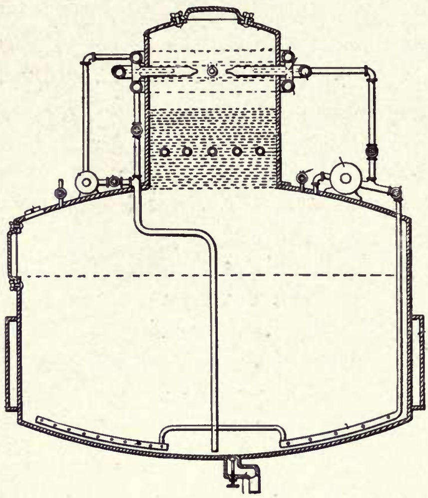


Fig. 35.

The oil 5 to be thickened or bleached is placed in the pan 6 (Fig. 36), the bottom of which forms one electrode, connected to the source of electricity by the conductor shown. The second electrode 8 having the terminal points 9 and fed through the conductor 10 is placed above the oil so that the discharge 11 acts upon the oily material.

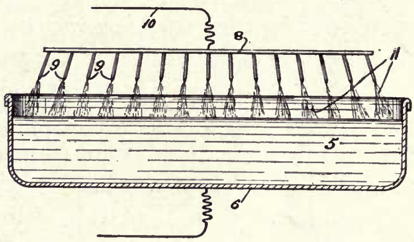


Fig. 36.

By the **Calvert** system the oil is submitted to violent agitation while under a hydrogen pressure of 250 pounds per square inch and at a temperature of 180° to 200° C., in a specially constructed autoclave having an electric motor (for stirring) enclosed in a chamber which is under the same hydrogen pressure as the autoclave proper.

* U. S. Patent 1,079,727, Nov. 25, 1913.

The motor chamber is substantially an extension of the autoclave, but is so far removed from the latter as to be unaffected by the heat.

The annexed illustration, Fig. 37, represents this type of oil hydrogenating apparatus which the Metropolitan Laboratories have put on the market. In the design is embodied the patented principle of enclosing the agitating motor in a chamber essentially an extension of the autoclave proper, and under the same gas pressure. By this arrangement the risk of leakage is entirely eliminated, and at the same time high stirring speeds are rendered possible without the frictional resistance which would be caused by shafts passing through glands, etc. The autoclave proper is the lower vessel shown in the illustration, and is enclosed in a heat-insulating jacket. The top vessel contains the electric motor, the intermediate tube through which the stirrer shaft passes being enclosed in a water jacket in the larger sizes. Current is conveyed to the motor by insulated screws on the top of the machine. On the right is the flue and the hydrogen feed pipe, the charging and discharging tube being shown on the left. For convenience in discharging the contents, in the smaller sizes the whole is mounted on trunnions.

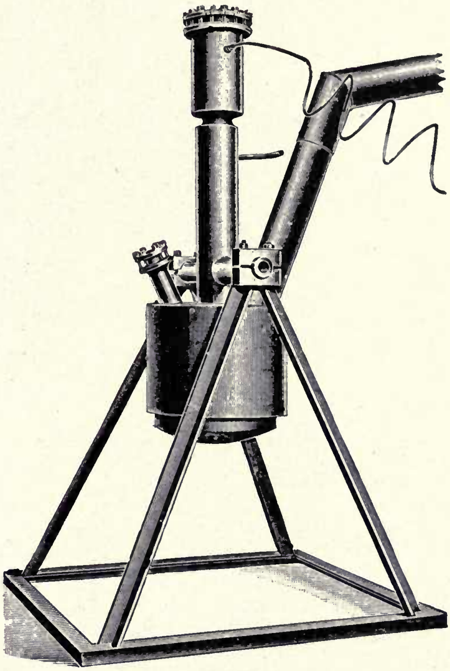


FIG. 37.

The oil is brought into a state of fine division by the stirrer blades, which cause the liquid to rotate against the inner side of the vessel, to which perforated baffle plates are fitted. The working pressure is 200 to 250 pounds per square inch, and the temperature about 185° C., but every machine is tested to 1000 pounds cold water and to 500 pounds gas at 200° C. The illustration represents a small size, suitable for oil laboratories, which stands about 4 feet high, but large units are also manufactured for working in batteries on a commercial scale.*

* Chem. Trade Jour. (1913), 618.

An apparatus for hardening oil, proposed by **Wilbuschewitsch,*** comprises the vessel R (Fig. 38) containing the fat to be treated and the vessel O containing the catalyst. Differentially-connected pumps AA' feed the oil and the catalyst into the mixing device B in which an intimate mixture of the oil and the catalyst is obtained. This mixture passes through a pipe G and the valve H into an autoclave J' which is provided with a spraying device C' consisting of a number of spraying nozzles so arranged that the oil and catalyst are uniformly scattered

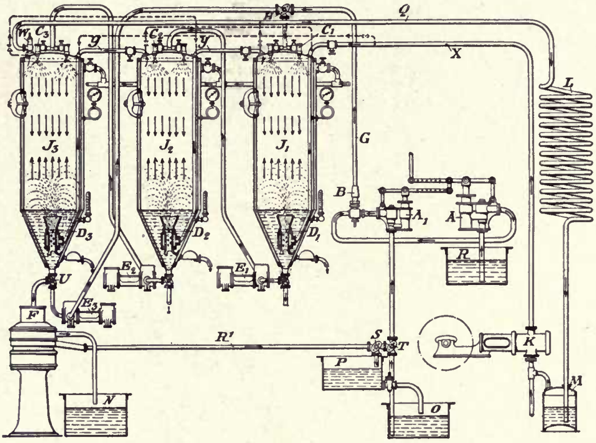


FIG. 38.

in finely-subdivided condition throughout the whole inner space of the autoclave. A compressor K forces hydrogen into the autoclave under a pressure of about 9 atmospheres. The pipe X extends from the upper part of the autoclave downward to the lower end of the same and is provided at its lower end in the conical lower part of the autoclave with an admission nozzle D'. By this spraying system an intimate contact of the oil mixture with the hydrogen is achieved on the counter-current principle. The autoclave is heated to between 100° to 160° C. according to the nature of the oil under treatment. The reduction by the hydrogen begins at the upper part of the autoclave. The partially reduced oil mixture collects in the conical part of the autoclave and is sprayed in the form of a fountain through the autoclave by the incoming hydrogen. The mixture is forced by pump E' into the second autoclave J^2. The hydrogen enters this autoclave through pipe Y and the action of the first autoclave is repeated. Any

* U. S. Patent 1,079,278, Nov. 18, 1913.

number of such autoclaves can be arranged in series or parallel to each other in accordance with the extent of reduction required. It is generally suitable to use one autoclave for each increase of melting point by 15° C. When the fat has attained the desired melting point which is ascertained by samples withdrawn from the autoclaves, the oil mixture is withdrawn through the valve *U* into the centrifugal apparatus *F*. Here the oil is separated from the catalyst. The finished reduced oil flows into the reservoir *N* while the catalyst is returned through the pipe *R′* and valves *S* and *T* to the vessels *O* and *P*. At first when the catalyst which Wilbuschewitsch employs is still quite fresh, he states that only a little of it is necessary — 1 per cent may be advantageously used. When, however, in the course of the operation its catalytic power decreases, correspondingly more of it must be used. The regulation of the quantity of catalyst may be attained by a suitable adjustment of the differential pump system. When the catalyst is completely spent it is allowed to flow out through the valve *S* into the reservoir *P* in order to be regenerated. The working is continued by introduction of fresh catalyst through the valve *T*. The hydrogen not consumed passes through the check valve *W* and pipe *Q* and cooling worm *L* into a vessel *M* filled with caustic soda lye where it is purified and then passes to the compressor and autoclaves.

Wimmer and **Higgins** * use as catalyzers organic metal salts such as the formates, acetates or lactates of copper, iron, nickel or cobalt. These require no special preparation before their use as catalytic agents; and it is claimed that impurities contained in the reducing gas employed in the treatment do not render these compounds ineffective. Wimmer and Higgins state that those processes in which finely-divided metals are employed in the treatment of unsaturated compounds call for the employment of intense mechanical agitation to obtain admixture of the catalysts and the liquid, or require the distribution of the metal over the outer surface of contact carriers such as pumice stone, kieselguhr, etc. By their process the compound to be reduced is mixed with the organic metallic salt, heated to a suitable temperature, and either a stream of the reducing gas is passed through the mixture, or the latter is subjected to an atmosphere of the gas in a closed vessel, while contact between the gas and the mixture or emulsion may be assisted by agitation. Under these conditions the saturation is said to take place comparatively quickly and the spent or partly spent catalytic agent can be removed by simple filtration after the operation.

* U. S. Patent 1,081,182, Dec. 9, 1913.

According to an example given, 100 grams of cottonseed oil are mixed with 1 to 5 grams of nickel formate (in concentrated aqueous solution or in the form of a powder). The mixture is warmed and a stream of hydrogen gas passed into the apparatus. During this time the temperature of the mass is raised to from 170° to 200° C. The duration of the treatment depends upon the quantity of the catalytic agent employed. The reduction may be carried out until the unsaturated compounds are quantitatively transformed into saturated ones. The mass is then filtered.

For this process they regard the metal salts, both normal and acid, of the mono- and polybasic carboxylic acids and hydrocarboxylic acids of the fatty groups as most suitable; the formates, acetates, propionates, butyrates, lactates, glycollates, oxalates, malonates, succinates, tartrates and citrates of nickel, cobalt, iron and copper are mentioned.

"The process may be modified in various ways. Thus, for example, the oil may be emulsified with the catalytic agent and simultaneously heated and have hydrogen or gas mixtures containing hydrogen passed through it in a suitable emulsifying apparatus; or the oil mixed with the catalytic agent may be brought into contact in a fine state of division with the hydrogen, as in a manner that has already been proposed. The reaction may also be accelerated by using the hydrogen under pressure or by impregnating the oil with hydrogen and then bringing it into intimate contact with the catalytic agent."

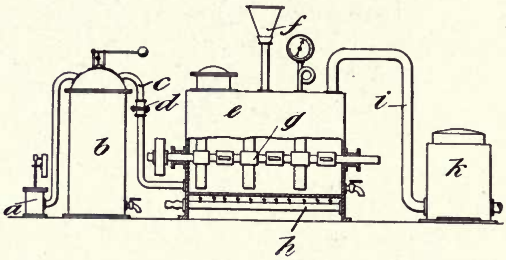


FIG. 39.

Fig. 39 is a view of an apparatus for carrying out the process. The gas is drawn by a pump *a* from a generator (not shown) and is forced by the pump into the pressure equalizer *b*. Thence the gas passes through a pipe *c*, into the receptacle *e* provided with a funnel *f* for introducing the mixture of catalyzer and oil. The mixing apparatus contains an agitator consisting of a longitudinal shaft provided with a series of revolving beaters *g*. In the base of the mixing apparatus is mounted a heater *h*. If water gas is used as the reducing agent, the portion of the gas, which has not been absorbed in the mixing apparatus, passes through a pipe *i* to a gas holder or collector *k*, and is then used for heating or power purposes.

A modified form of the inductor and tank shown in Fig. 26 is depicted in Fig. 40.*

In Fig. 40, 1 is a treating receptacle having the inlet 2 for oil or catalyzer; a hydrogen inlet 3; a back-flash tube 4; a draw-off valve 5; a steam heating coil 6; supporting members 7; and a catalyzer inlet 8 adapted to hold capsules of catalyzer;

* Ellis, U. S. Patent 1,084,203, Jan. 13, 1914.

11 is a pump connected with the lower part of the tank by the pipe 12 and having a discharge pipe 13 extending to an inductor 14 which is in communication by means of the inlet 15 and pipe 16 with the top of the treating receptacle 1. From the inductor the pipe 17 extends nearly to the bottom of the receptacle and terminates in a distributer 18 which is so arranged that the flow of material therethrough is both down and angularly against the bottom of the tank or receptacle.

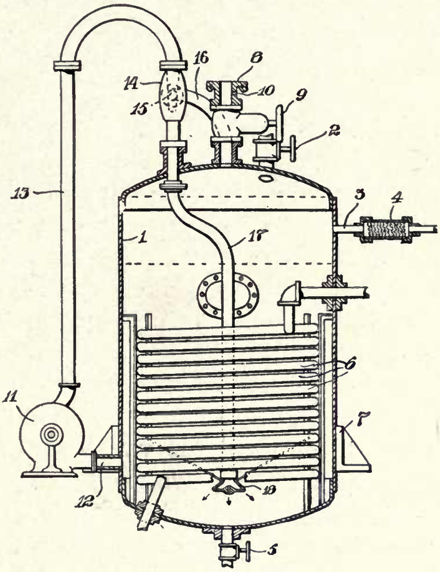


Fig. 40.

Bock* describes several forms of apparatus intended for hardening fats and fatty acids. One of these involves passing the fatty material along or through a porous plate containing catalyzer in the presence of hydrogen. Fatty acids may be hardened under a considerable degree of hydrogen pressure and subsequently the catalyzer may be freed from the acid by distillation under reduced atmospheric pressure. Reduced nickel on kieselguhr is used as a catalyzer.†

* Seifen. Ztg., 1914, 349.

† See also Seifen. Ztg., 1914, 421.

CHAPTER III

CATALYZERS AND THEIR ROLE IN HYDROGENATION PROCESSES

The Base Metals as Catalyzers

Catalyzers, those bodies which modify reaction velocity without stoichiometrical participation in the reaction, are destined to find another important industrial application in the hardening of oils.*

For present purposes a catalyzer may be simply, though less accurately, defined as a material or "exciter" which brings about a reaction between substances otherwise incapable of reacting, the catalyzer itself at the end of the reaction being unchanged. Thus fatty oil and hydrogen do not unite readily unless nickel or some other catalytic body is present to serve as a carrier or go-between to bring about the reaction.

The previous illustrations show the variety of methods proposed for mingling oil, hydrogen and catalyzer. Among these are several of excellent efficiency. But, after all, the virility, so to speak, of the process, depends on the *catalyzer*. With a powerful catalyzer the hydrogenation of oils becomes a rapid, simple procedure; almost, it sometimes seems, independent of the nature of the hydrogenating apparatus.

Catalyzers recognized as useful for the purpose are nickel and palladium, although platinum, copper, iron and other metals have been used to some extent. Nickel oxide, as stated, has been employed by Bedford and Ipatiew. Wimmer recommends organic salts of nickel, such as the formate, acetate or lactate.

As nickel is probably the most important of these catalyzers, in view of its efficiency and relatively low cost, it will be first considered.†

* Abel. Zeitsch. f. Elektrochem. (1913), 933–951, gives a bibliography on catalysis. Conroy, J. S. C. I., 1902, 302, discusses the industrial side of catalysis. See also Jobling, Chem. World (1914), 17; Agulhon, J. Agr. tropicale (1913), 375; Stern on Catalysis, Fortschritte d. Chem. Phys. u. Phys. Chem. (1913), 249. A very good review of the subject of oil hardening and the catalyzers employed for the purpose is contributed by Meyerheim, Fortschritte d. Chem. Phys. u. Phys. Chem. (1913), 293. Another review appears in the Bulletin of the Imperial Institute (1913), 660.

† Nickel is recommended as the best catalyzer for hardening whale oil, Seifen. Ztg. (1913), 1412.

The preparation of an effective nickel catalyzer requires considerable care. The oxide or hydrate of nickel is first obtained by ignition of nickel nitrate, or precipitation of nickel hydrate from, say, a nickel sulfate solution by the addition of an alkali. Obtained in this or in any other suitable manner, the next step is the reduction to metallic nickel. For this purpose the nickel is placed in a receptacle which may be heated controllably, and hydrogen gas is passed over the mass at a temperature ranging from 250° to 500° C. or so, until water is no longer evolved.

The most sensitive catalyzers are obtained by reduction at the lowest possible temperatures. Nickel begins to reduce below 220° C., but at 270° C. the reduction is not complete even after long duration of exposure to hydrogen. A temperature of 300° to 350° C. gives fairly complete reduction and is a satisfactory working range. The lower the temperature at which the nickel is reduced, the more sensitive it is to various external influences, hence the preparation of this catalyzer should be conducted not only with respect to degree of activity, but also with respect to longevity.

Nickel is easily poisoned by chlorine and by sulfur in the sulfide form.* The author has not experienced unfavorable results from the use of hydrogen gas passed through a wash bottle containing concentrated sulfuric acid and then conveyed directly to the catalyzer and oil. Traces of the acid were entrained by the gas, but the catalyzer remained in active condition during about two weeks usage under these conditions.

Copper is much less sensitive to poisons than nickel, but on the other hand it is much less active.†

Catalyzer made from the heavier forms of the oxide without supporting material, weight for weight, is hardly as efficient as when the active surface is increased by the use of a carrier. Hence we find many proposals for the production of catalyzers with a great diversity of carriers and extenders, ranging from pumice stone and kieselguhr to charcoal and sawdust.

* The albumin contained in animal and vegetable fats and oils is a source of sulfur-containing gases (Bedford and Erdmann, Jour. f. prakt. Chem., 1913, 426).

† Mailhe (Rev. gen. sci., 24, 650) describes the scientific and technical uses of active nickel as catalyst in the reduction of organic compounds and in the hydrogenation of oils. He also discusses the catalytic properties of finely-divided copper and the commercial possibilities of metallic oxides (especially ThO_2) as catalytic agents in processes requiring elimination of water (or water and hydrogen, depending on temperature) from organic compounds. Drawings are given, showing forms of apparatus. Much stress is laid on the maintenance of proper temperatures and on the use of pure hydrogen.

After reduction of nickel, as above, it should be kept out of contact with air as it is usually extremely pyrophoric and quickly loses much of its efficiency on exposure to the air.* Consequently when treating oil with such a catalyzer, it is advisable to free the treating apparatus from air by flushing with hydrogen; also it is sometimes beneficial to heat the oil and bubble hydrogen through it for a short time prior to the introduction of the catalyzer.

The use of nickel as a contact body by **Mond,**† in 1888, is of historical interest in view of present developments. Mond found that if carbonic oxide or gaseous hydrocarbons be brought into contact with metallic nickel at a temperature of 350° to 400° C., or with metallic cobalt at 400° to 450° C., decomposition takes place into carbon and carbonic acid or hydrogen, the carbon combining with the metal. If now steam, at a moderate temperature, be introduced, this carbon combines with oxygen to produce carbonic acid, with simultaneous formation of free hydrogen. These various reactions take place simultaneously when the steam is passed through the apparatus along with the carbonic oxide or hydrocarbon, the ultimate products being carbonic acid and hydrogen. The former can be eliminated by any suitable means, such as by washing with milk of lime. The cobalt or nickel surfaces may be obtained by *impregnating pumice stone with a solution of the metal,* and reducing.‡

The Mond and Langer British Patent 12,608, of 1888, is entitled Improvements in Obtaining Hydrogen. From the specification the following is quoted:

"By the distillation or incomplete combustion in the presence or in the absence of steam, oil, lignite, wood, coke, animal carbon or organic substances in general, gases are obtained which consist chiefly of hydrogen, carburets of hydrogen, monoxide and dioxide of carbon and a greater or less quantity of nitrogen. The object of our invention is to eliminate from these gases the monoxide of carbon and the carburets of hydrogen, and at the same time to increase the amount of hydrogen contained.

"If a mixture of monoxide of carbon or carburet of hydrogen and steam be heated to white heat in the presence of firebricks or of oxide of iron, the latter is decomposed and the carbon of the gases is oxidized to carbon dioxide and the hydrogen set at liberty. The high temperature required for this reaction renders it of little profit and it is difficult to produce it on an industrial scale. We have found that if monoxide of carbon and hydrocarburets be placed in contact with metallic nickel or

* Wimmer and Higgins (Seifen. Ztg. (1913), 556) prepare catalyzer by reducing the active material while it is enveloped in a protecting material, oil being recommended for this purpose.

† British Patent 12,608, Sept. 1, 1888.

‡ The use of nickel in the catalytic reduction of carbon monoxide to methane is set forth in U. S. Patents to Elworthy 738,303, Sept. 8, 1903; 777,848, Dec. 20, 1904; and 943,627, Dec. 14, 1909.

cobalt at a temperature not exceeding a red heat, these gases are decomposed into carbon and dioxide of carbon on the one hand and hydrogen on the other; the free carbon so formed placed in contact with steam at a moderate temperature decomposes the latter and forms dioxide of carbon and hydrogen.

"If the steam and the gases are mixed from the commencement, the two reactions take place simultaneously and the result is a gas practically free from monoxide of carbon and hydrocarburets. It is quite possible to attain our object by carrying out consecutively the two above-mentioned reactions and by repeating them continually with the same quantity of nickel and cobalt which will always be regenerated. We prefer, however, to carry out these two reactions simultaneously, at the same time employing the least possible amount of nickel and cobalt; with this object we spread the aforesaid metals on an indifferent refractory and porous material. For example, we saturate pieces of pumice stone with a solution of chloride of *nickel* or *cobalt*, dry and reduce at a higher temperature with hydrogen.

"In carrying out our invention industrially we lead the gases with an excess of steam into retorts or cylinders fixed in a suitable furnace and containing pieces of pumice stone impregnated with nickel or cobalt as above mentioned. When nickel is used, the reaction takes place at a temperature of 350° to 400° C. If cobalt be used, at a temperature of 400° to 450° C. The reactions which take place between the gas and the steam produce heat so that the given temperature once reached the reaction goes on of itself without need of external heating.

"It may, however; be advantageous to use gases or steam or both, heated to a suitable temperature before they are placed in the retorts. The gases so treated contain little or no monoxide of carbon. The carbonic acid can be separated in any known manner, such as by passing the gases through lime or caustic alkali.

"The foregoing process differs entirely from the plan of using an easily reduced oxide and oxidizing the carbonic oxide or hydrocarbons by means of that oxide at a bright red heat, as in our case no oxide is used, but a metal having but little affinity for oxygen, but a considerable affinity for carbon. The metal deprives the carbonic oxide of a part of its carbon and gives the latter up to the oxygen of the steam. This is done at a heat much below that at which oxide of iron or other like oxide would give up its oxygen."

Mond and Langer lay claim to the process of obtaining hydrogen by means of gases containing carbon monoxide with or without hydrocarbons which consists in treating such gases with metallic nickel or cobalt and with steam and separating from the hydrogen the carbonic acid resulting from such a treatment.

They also claim the use of pumice stone or other similar porous substance impregnated with one or more salts of cobalt or nickel so as to provide, when reduced, an extended metallic surface with only a small amount of actual metal.

These extracts are given because of the use by Mond and Langer, in 1888, of reduced nickel or cobalt on porous refractory material for catalytic purposes, although, to be sure, the object of the process was to produce hydrogen rather than to cause its combination with unsaturated bodies.

Carbon and hydrogen combine with difficulty, especially to form methane. At the ordinary pressure in the presence of nickel oxide, reduced nickel or a mixture of nickel and alumina, and up to 625° C., there is no formation of methane. Under great pressures its synthesis only occurs above 500° C. in the presence of the above substances or mixtures, and so much the better as the temperature becomes greater. In the presence of water and nickel, methane is decomposed at 500° C. into hydrogen and carbonic acid. The inverse reaction, i.e., reduction of carbonic acid to methane

in the presence of nickel and an excess of hydrogen at ordinary pressure, occurs at 450° C. Results are the same with nickel oxide. (Chem. Trade Jour., Oct. 25, 1913, 414.)

At ordinary pressure no methane is formed by combination of its elements in the presence of catalyzers such as nickel or nickel oxide, but under high pressures and at a temperature of 510° to 520° C., methane is formed. (Ipatiew Chem. Ztg. Rep. (1914), 15.)

Acetylene is converted into ethylene by treatment with hydrogen under pressure in the presence of catalyzers. The Elektro Chemische Werke G. m. b. H. (Zeitsch. f. angew. Chem. (1913), ref. 644) find that the production of ethylene from acetylene and hydrogen on a commercial scale is difficult, due to the gradual loss in the efficiency of the catalyzer. Even though the usual precautions are taken to remove the recognized poisons, such as hydrogen sulfide, sulfurous acid, chlorine and the like, there still remain in the gas certain impurities which cannot be eliminated by the usual absorption reagents. Accordingly it is recommended to wash the hydrogen with concentrated sulfuric acid, then to pass it over solid caustic soda, which treatment is said to remove the troublesome bodies. To effect the combination of the unaltered ethylene and hydrogen in the gaseous mixture resulting from the passage of these gases over a catalyst, the product is again passed over the catalyst under pressure. The reaction is stated to be quantitative and instantaneous. Nickel or a metal of the platinum group may be used as a catalyst. (German Patent 265,171, Oct. 16, 1912.)

From a very lengthy paper published by **Sabatier** and **Senderens** * the following items on the preparation and use of catalyzers have been noted.

Access of air to the catalyzer oxidizes it and destroys or diminishes its activity. To prepare catalytic material one should use an oxide quite free of chlorine or sulfur. Good results are obtained by dissolving the metal in pure nitric acid and forming the oxide by calcination at a low red heat. Reduction of the oxide should be with pure hydrogen, free from chlorine or sulfur. Reduction should take place at a low temperature, always below a red heat, or the catalyzer will not be efficient.

Nickel reduced at a red heat has practically no activity. At 300° C. it gives a *very* active material if used *immediately*. It is better, however, to employ a temperature of 350° C. Copper is best treated at 300° C., while cobalt † requires 400° C. Iron is difficult to reduce. At 450° C. some 6 or 7 hours are required to completely transform the oxide into the metal. Nickel and copper are actually reduced near 200° C., so even if some oxidation of the catalyzer were taking place,

* Ann. de Chim. et de Phys., 1905 (4), 319.

† The reduction of cobalt oxides by hydrogen and carbon monoxide at different temperatures is described by Kalmus. (Jour. Ind. Eng. Chem. (1914), 112–114.) For some metals the minimum temperature of reduction is lower with carbon monoxide than with hydrogen (Fay and Seeker, J. Am. Chem. Soc., 1903, 641).

because of the presence of oxygen in the hydrogen gas, immediate reduction would occur thereafter.

The hydrogen employed is dried with sulfuric acid, is then passed through a tube of Jena glass filled with copper turnings maintained at a low red heat and finally goes through a long tube filled with fragments of caustic potash.

The catalyzer should be prepared in the tube in which the material to be hydrogenated is treated.

For high temperatures a copper tube heated in a bath of equal parts of sodium and potassium nitrate (which melts at 225° C.) may be used.

With regard to the life of the catalytic material the investigators state that there are three periods noticeable.

1. A short period when the catalyzer is becoming accustomed to the atmosphere of hydrogen and the body to be treated.
2. A period of normal activity.
3. A period of decline.*

The second or normal period is generally very long, if no trace of bodies capable of altering the surface of the metal is present. For example, with a nickel catalyzer good results were secured for one month in the transformation of benzene into cyclohexane. The operation was interrupted each night and resumed the next morning. The slight oxidation over night did no harm as the oxide was reduced again the next day at the temperature of working, which was 180° C.

If in the hydrogen there is a trace of certain bodies, the action of the catalyzer is rapidly suppressed. Even tiny traces of chlorine, bromine, iodine or sulfur paralyze the nickel. Nickel obtained from oxide carrying a little chlorine is usually devoid of activity. Nickel from oxide containing a trace of sulfur is likewise inefficient. The presence in the hydrogen of even faint traces of hydrochloric acid, hydrogen sulfide or selenium compounds produces the same disastrous effects. Traces of bromine in some phenol which was used paralyzed the nickel. The same thing happened with benzol containing this compound.

Catalyzers finally lose their efficiency either by traces of poisons or by a deposit of tarry or carbonaceous material on the catalyzer particles. On dissolving spent nickel in hydrochloric acid a fetid gas is evolved and brown carbonaceous material is deposited.

According to Sabatier and Senderens the operation should be conducted to prevent *liquid* coming into contact with catalyzer. The temperature limits practically are those imposed by maintaining the

* These periods are similar to those noted in the case of ferments.

substance in a state of vapor. Too high temperatures sometimes cause decomposition. Benzene becomes cyclohexane at temperatures up to 240° C., but at 300° C. the cyclohexane gives benzene and methane:

$$3\,C_6H_{12} = 2\,C_6H_6 + 6\,CH_4.$$

Copper and platinum work well in case of ethylene groups, but are not satisfactory for hydrogenation of the aromatic ring. Nickel is effective on the latter.*

Some peculiarities of catalytic nickel have been recorded by **Senderens** and **Aboulenc.**† These investigators state that the temperature at which nickel oxide is reduced by hydrogen is found to depend on the mode of preparation and treatment of the oxide used, there being also a considerable difference between the temperature at which reduction commences and that at which it is complete. Complete reduction is not effected below 300° C., but the mixture of metal and oxide thus obtained is more active than the metal prepared by total reduction at a higher temperature, the activity of reduced nickel being diminished by heating to a comparatively high temperature, although, at the same time, its catalytic properties are rendered more permanent. Pyrophoric nickel, when heated in the air, furnishes an oxide which is reducible at a comparatively low temperature, and reduced nickel of impaired activity may be restored, therefore, by oxidizing it and again reducing.

According to Moissan the protoxide of nickel in hydrogen at 230° to 240° C. blackens and reduces, giving a body pyrophoric at ordinary temperature. Muller states the protoxide of nickel at 210° to 214° C. in hydrogen loses 11 to 14 per cent of oxygen, apparently giving nickelous oxide which corresponds to a loss of 10.7 per cent oxygen. At 270° C. it passes into the metallic state. For hydrogenation the anhydrous or hydrated oxide of nickel supported on pumice is reduced at 270 to 280 degrees (Brunel); 280 degrees (Leroux); 255 to 260 degrees (Godchot); 245 to 250 degrees (Darzens).

Senderens and Aboulenc, however, after a protracted investigation, recorded results which in brief are as follows:

(*a*) Anhydrous nickel oxide: This oxide becomes green a little above 200° C. in presence of hydrogen, but the reduction commences only at about 300° C. and is slow at 330° C. It goes on much faster

* Sabatier has reviewed the subject of catalytic action in organic chemistry, the publication appearing as Vol. III of the Encycl. de Science Chimique applique aux arts industriels.

† Bull. Soc. Chim. (1912), 11, 641.

at 380° C. up to two-thirds the amount of water which should be evolved. There reduction stops. To get complete reduction the temperature has to be raised to 420° C. The nickel obtained is pyrophoric. It serves very well for the hydrogenation of carbon monoxide, carbon dioxide, benzene and toluene, but does not work well with the phenols.

(*b*) Nickel oxide obtained by calcination: This shows a great resistance to reduction. It is necessary to raise the temperature to 420° C. to obtain two-thirds of the water of theory and to a red heat to secure complete reduction. Heated to this last-named temperature the product is inactive even with carbon monoxide which is very easily hydrogenated. It is pyrophoric, however. The efficiency of nickel as a catalyzer does not depend on any pyrophoric property. Non-pyrophoric nickel has been prepared which is a good catalyzer. Reduction of the oxide (*b*) at 420° C. gives about one-third oxide with two-thirds metal. This mixture is active and pyrophoric. It easily converts water gas into methane.

(*c*) Hydrate of nickel: Introducing hydrate, prepared in the laboratory, into the tube used for reduction, the dehydration was very slight at 200° C., while at 230° C. reduction took place and at 270° C. dehydration and reduction progressed, but rather slowly. In another experiment the same "hydrate" was reduced after gently heating in a crucible to remove the water. The reduction presented the same variations commencing about 230° C. and progressing very gently up to 270° C. at which point water was given off regularly for 6 hours in an amount corresponding to one-third the total expected from the reduction of the oxide. At 300° C. two-thirds of the water was collected and at 320° C. the remainder was obtained after treatment for several hours.

Another hydrate of nickel furnished by a chemical supply house was more difficult to reduce, not giving off as much water as the preceding at temperatures 20 to 30 degrees higher.

Oxides of pyrophoric nickel: These may be obtained by letting pyrophoric nickel oxidize in a thin layer in the cold or by heating. In the cold the oxidation is variable; when heated the reaction is complete in a moment. The oxides obtained in this manner commence to reduce at a temperature much lower than those from which the pyrophoric nickel was derived. For example, the oxide resulting from the simple exposure to the air of the pyrophoric nickel obtained from the hydrate (*c*) was reduced at 210° C. by hydrogen, giving about one-half the theoretic water.

The oxide obtained by moderate calcination in the air of this same

pyrophoric nickel takes up hydrogen at 250° C. giving off half the theoretic water; after which, to complete the reduction it is necessary to raise the temperature as in the preceding case.

The anhydrous oxide (*a*) commenced to reduce at 300° C., reduction was slow at 330° C. and normal only at 380° to 420° C. The pyrophoric metal which results when this material is heated in contact with air furnishes an oxide of which one-third is reduced at 280° C. and half at 320° C. The activity of the nickel reduced from these oxides is at least equal if not superior to that obtained by the reduction of the normal oxide.

When the nickel begins to weaken in catalytic effect it is necessary only to oxidize and then reduce it, in order to have the catalyzer completely regenerated.

Passivity of nickel as a catalyzer: If used to hydrogenate phenol for a day or two it will then hydrogenate cresol, but if used for a month on phenol it will not be active on cresol, although still active on phenol. By oxidizing and then reducing, the material is very active on cresol.

Anhydrous oxides and hydrates of nickel cannot be completely reduced to the metal at 300° C., but a mixture of the metal and oxide results. It is nevertheless true that such mixtures are more active than if complete reduction with corresponding elevation of the temperature had taken place.

Two stages of oxidation, derived from the same pyrophoric nickel of which in one case the reduction was arrested at 250° C. when one-half the oxide remained, and in the other case the material was heated up progressively to 350° C. to give total reduction, were tested. The latter hydrogenated xylenol normally, while the former gave a hydrocarbon. To evade this destructive action in a number of cases the investigators heated the nickel after reduction to a higher temperature to diminish its activity and conserve its life as a catalyzer.*

* Padoa and Fabris (J. S. C. I., 1908, 1083) showed that at ordinary pressure indene is not capable of combining with hydrogen in presence of reduced *nickel* at 300° C., but that at 250° C. two atoms of hydrogen are taken up. Ipatiew (J. Russ, Phys. Chem. Soc. (1913), **45**, 994) finds that in presence of *nickel oxide*, indene unites with hydrogen at 250° to 260° C. and 110 atmospheres, yielding the hydrocarbon octohydroindene. The nature of the metal of which Ipatiew's high-pressure apparatus (J. S. C. I., 1911, 239) is constructed is found to exert an influence on the hydrogenation, in presence of cuprous oxide, of compounds containing ethylene linkages. Thus, in an iron tube, amylene (trimethylethylene) is readily converted into isopentane, while in a copper tube the reaction is incomplete, an equilibrated mixture of amylene, hydrogen and isopentane remaining:

$$C_5H_{10} + H_2 \rightleftarrows C_5H_{12}.$$

In an iron tube and in absence of cupric oxide, no hydrogenation occurs. Similar

Several types of catalyzers have been proposed for oil hardening and in some cases processes have been prescribed for operation with specific catalyzers. From the standpoint of the support or carrier for the primary active material catalyzers may be divided into several well-defined groups, each exhibiting characteristic properties. The classification embraces:

Classification of Catalyzers

Group A

I. Carrier porous, inert and coated but is not impregnated with catalytic metal.

II. Carrier active, serving as a secondary catalyzer or feeder, is coated but not impregnated with catalytic metal.

Group B

I. Carrier non-porous, inert and is fairly evenly coated with catalytic metal.

II. Carrier non-porous, inert and instead of being coated is punctated with metal nodules.

III. Carrier non-porous, active and is fairly evenly coated with catalytic metal.

IV. Carrier non-porous, active, serving as a secondary catalyzer or feeder and instead of being evenly coated is punctated with metal nodules.

Group C

I. Carrier porous, inert and is impregnated with catalytic metal.

II. Carrier porous, active, serving as a secondary catalyzer and is impregnated with catalytic metal.

Other subdivisions follow if the catalytic material is used in a coarse condition or in a finely-divided state, etc. Superficially treated or coated carriers are regarded as more desirable for treating liquids, while the porous impregnated varieties find a better field of utility in the hydrogenation of gases or vapors which in admixture with hydrogen are capable of penetrating porous bodies into which viscous liquid compounds would not readily diffuse.

results are obtained with hydro-aromatic compounds. Further, hydrogenation in an apparatus of phosphor bronze in presence of reduced copper results in the establishment of an equilibrium,. while, if iron turnings are also present, hydrogenation proceeds to an end. The slight catalytic activity of reduced copper in copper tubes may be regarded as due to poisoning of the catalyst; or the use of cupric oxide in iron tubes may result in a conjugated catalytic action.

Ipatiew (Chem. Centralbl. (1906), II, 87) found alumina to act as a dehydrogenating catalyzer on various bodies.

CHAPTER IV

THE BASE METALS AS CATALYZERS

Nickel Catalyzers — Continued

Nickel oxide catalyzer is recommended by **Bedford** and **Erdmann***, as preferable to the metallic forms and some of the features claimed for this material are noted in the following: They indicate that the hydrogenation of oils by means of finely-divided nickel, although now worked on a commercial scale, has the disadvantage that the catalyst

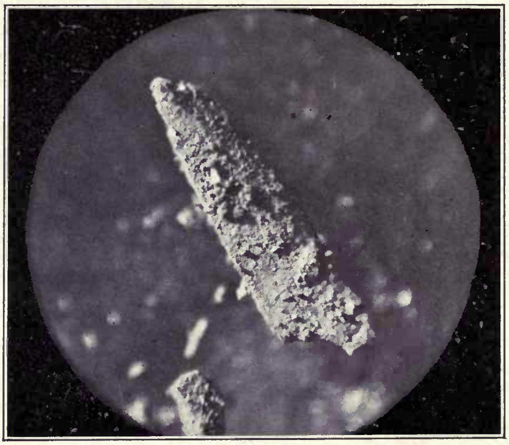


Fig. 41. — Photo-micrograph of a particle of crushed glass coated with nickel oxide (equivalent to 10 per cent of metallic nickel).

is extremely sensitive to small quantities of air and to traces of chlorine and sulfur compounds, which latter may be developed from protein, always present in vegetable and animal oils. Oxides of nickel are capable of acting as hydrogen carriers for the hydrogenation of oils at atmospheric pressure, and possess the advantage over metallic nickel of being relatively insensitive to gases containing oxygen and sulfur compounds; moreover hydrogenation proceeds with much greater velocity than with metallic nickel. Any one of the oxides of nickel may be used, viz., nickel sesquioxide, nickel monoxide or nickel sub-

* J. Prakt. Chem. (1913), 87, 425.

oxide;* with the sesquioxide and monoxide a temperature of about 250° C. is required, but with nickel suboxide 180° to 200° C. is sufficient. When the higher oxides of nickel are used they become partially reduced to the suboxide which is said to form a colloidal suspension in the oil. Hence a nickel oxide catalyst becomes more active after it has been used, owing to the formation of the suboxide. No reduction to metallic nickel occurs during the hydrogenation process, although in absence of oil, reduction of nickel oxides to metallic nickel by hydrogen takes place at 190° C. Nickel suboxide may be distinguished from metallic nickel by its lack of electric conductivity and by its inability to form nickel carbonyl when treated with carbon monoxide under pressure at a moderate temperature. Other metallic oxides (e.g., copper oxide, ferrous oxide) are also capable of acting as catalyzers in the hydrogenation of oils, but do not act so well as nickel oxide. The activity of nickel oxide is increased by small quantities of the oxides of aluminium, silver, zirconium, titanium, cerium, lanthanum and magnesium. Nickel salts of organic acids do not act as catalysts, but in presence of the heated oil are decomposed by hydrogen, yielding nickel oxides and, under certain conditions, also metallic nickel; the resultant nickel material then acts as a catalyst. Nickel formate in the presence of the heated oil is reduced by hydrogen to nickel suboxide at 210° C., while at 250° C. metallic nickel is also produced. In carrying out the hydrogenation, the oil is placed in a cylindrical copper vessel fitted with an agitator, and heated in an oil bath to 180° C. while a slow current of hydrogen is passed through. A small quantity of nickel oxide is then added, the temperature is raised to 255° to 260° C., a further addition of the catalyst is made and the supply of hydrogen is increased. The hydrogenation is controlled by examining test-samples of the oil as to melting point and iodine value. The oil becomes black possibly owing to the formation of "col-

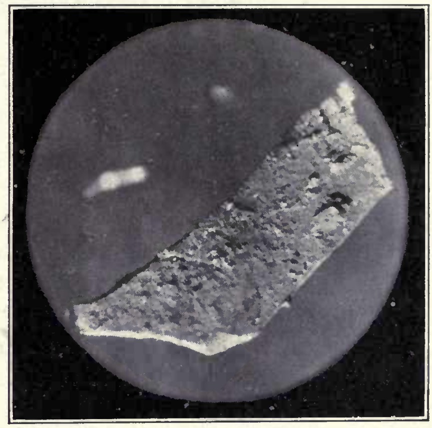


FIG. 42. — Photo-micrograph of a particle of crushed glass coated with 10 per cent of reduced nickel.

* Compare Moore, Chem. News (1895), 7182. Böhm (Seifen. Ztg. (1912), 1044) briefly discusses oxide catalyzers. See also Soap Gazette and Perfumer, 1913, 107.

loidal" nickel suboxide, which passes through a filter-paper, but can be removed by centrifuging. Nickel soaps are formed only to a slight extent, and probably in consequence of a secondary reaction during the cooling. The hydrogenized fat is free from hydroxy-acids. The catalyst after use contains some organic matter apparently composed partly of nickel palmitate or stearate, and other substances, one of which probably is nickel carbide. The process is easy to control if pure hydrogen is available, and in an experimental plant of 1 ton capacity Bedford and Erdmann report that more than 100 tons of different oils have been hardened by hydrogenation in the manner described.

Nickel oxide catalyzers have been made the subject of a number of patents.

English Patent 4702, of 1912, to Boberg and the *Techno-Chemical Laboratories, Ltd.*, London, proposes to prepare catalyzer through the reduction of a metallic compound such, for example, as ignited nickel carbonate, the reduction taking place with hydrogen under such conditions that the nickel contains one or more suboxides, or when nickel is employed a compound is formed which contains less oxygen than the ordinary oxide NiO.*

The observation is made that in the reduction of ignited nickel carbonate by hydrogen the product obtained is just so much more efficient catalytically the lower the temperature at which the reduction takes place, because of the suboxide formed. The catalyzer apparently also contains some hydrogen. The preparation of the catalyzer is carried out by passing ignited nickel carbonate, free from injurious impurities, continuously in a slow stream through an inclined rotary cylinder, which is heated in part or throughout its length, while hydrogen is allowed to flow through in an opposite direction. By suitable regulation of the influx of the material as well as the proper regulation of the temperature, the reduction may be carried out in such a manner that one obtains a catalyzer which is partly or mainly composed of the suboxide. The most suitable temperature is between 230° to 270° C. and the length of the heating operation must be just so much more prolonged the lower the maintained temperature. Unnecessarily long heating must be avoided otherwise the reduction goes too far which causes a diminution in catalytic activity. The catalyzer so obtained can be used immediately for oil hardening or it may be pre-

* The proposal by **Boberg** to prepare a catalyzer from nickel carbonate by ignition and reduction to form a mixture of nickel and its suboxide is criticized by the editor of the Chemiker Zeitung (Chem. Ztg. (1913), 481) as offering nothing novel in view of Bedford's disclosures in English Patent 29,612, 1910.

served in contact with air where it oxidizes very slowly, provided local over-heating is avoided.

One can also collect the catalyzer in water, filter and dry in the air; or it can be collected in an atmosphere of hydrogen which is gradually displaced by air.

The production of suboxide catalysts is also carried out by reducing nickel oxide as completely as possible and then controllably oxidizing the product in any suitable way as with air or oxygen diluted with an indifferent gas, such as carbon dioxide, so that the introduction of oxygen can progress without local overheating. Such oxidation can go on between 300° to 600° C.

The degree of catalytic activity of a metal oxide depends not only on its chemical but also on its physical properties. It is known that metal catalyzers, such as nickel, cobalt and iron, require very fine division for effective action. The same is also true of the oxides of these metals. The German Patent to **Erdmann** and **Bedford** (260,009, 1911) relates to oxide catalyzers in a voluminous form. The patentees state that metal oxides may be obtained in the form of an especially finely-divided voluminous material if one takes a concentrated aqueous solution of the nitric acid salt from which the oxide is to be made, mixes with it a water-soluble organic compound rich in carbon and then subjects the mixture to combustion by allowing it to fall, drop by drop, into a heated vessel. The strong evolution of gas which thus takes place, due to the combustion of the organic compound and simultaneous decomposition of the nitrate, produces nickel oxide in a very voluminous form. Especially recommended for this purpose are the sugars and carbohydrates, for these when heated by themselves produce a strongly-swelling carbonaceous mass.*

As an example Erdmann and Bedford state that nitric acid of 1.42 specific gravity is diluted with an equal volume of water. Pure metallic nickel is introduced. After the reaction is complete the solution is heated for two hours with an excess of nickel in order to completely neutralize the nitric acid and to separate any iron present as a precipitate of iron hydroxide. The clarified nickel nitrate solution is evaporated to specific gravity of 1.6 and to one liter of this fluid, corresponding to 250 grams of nickel, 180 grams of powdered cane sugar are introduced. This solution is allowed to run in portions into a muffle heated to a low red heat. Each portion is heated until no

* The use of sugar or gum in a somewhat similar manner has been described by Schroeder (J. S. C. I., 1902, 344 and British Patent 10,412, 1901), who found it possible to increase the porosity of catalytic material by ignition with such carbonaceous matter, so as to form blowholes or bubbles in the catalytic mass.

more red vapors depart, when the voluminous nickel oxide which is formed is removed from the muffle and a fresh portion of the solution is introduced.

In place of cane sugar other varieties of sugar may be applied and also water-soluble starch, dextrine, gum, tartaric acid or other water-soluble organic acid substances which are rich in carbon.

In a similar manner the oxides of cobalt and iron or other catalytically-active oxides may be brought into a voluminous form.*

It is the belief of **Erdmann** † that the oxide catalysts are superior to metal catalytic material, because the former not only have strongly marked catalytic properties but they are more stable than the latter. Erdmann refers to prior investigations of Ipatiew who worked with various organic compounds other than fats, employing nickel oxide and hydrogen under very high pressure; while in the present case fatty material, it is claimed by Erdmann, is smoothly hydrogenated under ordinary atmospheric pressure. For example, linseed oil or any other fatty oil may be heated with one-half to one per cent of nickel oxide, such, for example, as may be obtained by calcining pure nickel nitrate at a low red heat. The temperature of the linseed oil is raised to about 255 degrees and a stream of hydrogen is passed through the oil when it is observed that the nickel oxide and oil mixture becomes deep black and the oxide appears to undergo subdivision and possibly transformation into a colloidal state, the solvent acquiring an ink-like appearance. At the same time hydrogen is absorbed and the oil is hydrogenated.

This "colloidal" form of nickel oxide catalyzer, which apparently has not been observed with metallic nickel, is regarded by Erdmann as of great importance in this art because it enables a finely-divided catalyzer of an effective nature to be so easily prepared. When the hardening process is finished the nickel oxide catalyzer clots and collects so that it may be separated readily from the hardened fat.

The analyses of the hardened products of linseed, peanut and sesame oil show that by the process an approximately pure glyceride of stearic acid is produced without any trace of oxy fatty acid impurity.

Nickel soaps form in the presence of free fatty acid only in an inconsequential way to an amount of about $\frac{1}{100}$ of 1 per cent or so. This slight amount is said to remain along with the catalyzer in an undissolved state.

* Suboxide of nickel is prepared for catalytic purposes, according to Bedford and Williams (J. S. C. I., 1914, 324), by heating a mixture of nickel oxide or an organic salt of nickel with oil in a current of hydrogen.

† Seifen. Ztg. (1913), 605.

The whole hardening process, when pure hydrogen is at one's disposal, is so simple with reference to the apparatus required, and operates so smoothly that the shifting from the laboratory experiments to work on a large scale is stated to have offered no difficulties.

In one experiment carried out by *Bedford* and *Erdmann* * 3 grams of freshly prepared nickel oxide were added to 30 grams of cottonseed oil and treated with hydrogen at 260° C. until the oxide had become black in color and very finely divided. The solidifying point of the fat was then 48° C. The mixture was cooled to 185° C., 270 cc. of cottonseed oil added and a strong current of hydrogen passed through the oil and catalyzer (maintained at 185° C.), for one hour when the solidifying point was found to be 45° C.

Another interesting question to which reference has already been made is whether or not nickel oxide in oil is reduced to metallic nickel by hydrogen, and whether any finely-divided metal which might arise in this manner is a carrier of hydrogen.†

While nickel oxide (NiO or N_2O) yields nickel in an hydrogen atmosphere at 260 degrees and even in fact as low as 190 degrees, the behavior of these bodies, according to Erdmann, is very different when they are immersed in oil. In the latter case the oil acts as a protective element and hinders or prevents complete reduction. The reduction goes no further than the suboxide stage, and Erdmann believes that some sort of an addition compound is formed with the unsaturated oil. If the catalyzer is removed from the hardened fat and entirely freed from the latter by extraction with benzol, the used catalytic material is obtained in the form of a soft black powder which is more or less strongly magnetic, but which does not possess any conducting power for electricity.

A great number of analyses have shown that the nickel content lies between nickelous oxide and a form of suboxide described by Moore.‡ Not the slightest trace of metallic nickel is found in the used catalyzer if the fatty oil is free from strongly reducing substances such as aldehydes or formic acid.

* Jour. f. prakt. Chem., 1913, 446.

† The possibility of nickel oxide and carbonate becoming reduced during hydrogenation operation, so as to actually yield a metallic catalyzer similar to that covered by the Leprince and Siveke basic patent, is considered by Mayer (Seifen. Ztg. (1913), 1224) who also discusses the situation in Germany respecting patented processes of hydrogenation.

Professor Erdmann (Seifen. Ztg. (1913), 1325) discusses the scope of the Leprince and Siveke German Patent 141,029 corresponding to the Normann British Patent 1515, 1903, especially with regard to the use of nickel oxide catalyzer in the form employed by Bedford and Erdmann.

‡ Chem. News, 71, 82.

The absence of metallic nickel* is rather definitely shown through the indifferent electrical conductivity of some used nickel oxide catalyzer from which the fat had been removed, the oxide being pressed into block form for the purposes of such test. A control test made with catalyzer which before use had received an addition of a few per cent of freshly-reduced nickel showed, under like circumstances, a relatively high electrical conductivity. Also the very different behavior of carbon monoxide toward metallic nickel and nickel oxide indicates the non-metallic nature of the used nickel oxide catalyzer.

So in two ways it is alleged to have been shown that under normal conditions of the process of hydrogenation, nickel oxide is not reduced to metallic nickel. According to Erdmann, after numerous comparative tests, a great advantage of the process over those made known up to this time has been established. The fact that nickel oxide catalyzers experience a partial reduction to nickel suboxide brings up the question as to whether or not the suboxide is the only oxide of nickel which is capable of transferring hydrogen to unsaturated compounds.

In the application of the higher oxide the first phase of the hydrogenation which takes place at 250 degrees is that of the formation of magnetic suboxide, and the once-used nickel oxide catalyzer possesses more marked activity than the unused. With such a once-used catalyzer hydrogenation progresses with much greater rapidity and also at an essentially lower temperature. After use eight times the nickel oxide catalyzer was still active.

Erdmann prepared Moore's suboxide through electrical reduction from a solution of nickel potassium cyanide. This he found possessed the properties stated by Moore, namely, it was magnetic, reduced nitric acid, developed hydrogen with mineral acids and showed no electrical conductivity. The compound, both in water and in oil, showed colloidal properties. When introduced into hot cottonseed oil it distributed itself through the oil in the form of a very fine suspension which colored the oil black, and treatment with hydrogen at 210° C. indicated that the compound even at that relatively low temperature was an excellent reduction catalyzer.

In passing, it may be mentioned that other oxides besides nickel have been found to possess the property of transferring hydrogen.

* Meigen and Bartels (J. prakt. Chem., 1914, 301) consider the views of Erdmann, regarding the formation of nickel suboxide when employing an oxide catalyzer, to be untenable, and conclude that metallic nickel is formed under the conditions established by hydrogenation. Experimental studies in support of this position are detailed. From the analytical results, the electrical conductivity and the observed formation of nickel carbonyl, Meigen and Bartels consider metallic nickel to be indicated, contrary to the views of Erdmann.

This has been noted with copper and iron oxide. Osmium tetroxide has been found by Lehmann to effect hydrogenation while in itself becoming converted into colloidal osmium dioxide.

A comparison has been made by Erdmann between oxide catalyzers and organic-salt catalyzers, such as the formate, acetate, oleate and other similar salts which have been studied in connection with oil hardening, and Erdmann has reached the conclusion that these salts do not act directly as catalyzers. In order to effect hardening it is necessary to break down the organic salt. It does not in itself possess the property of acting as a hydrogen carrier. So long as it remains unchanged no hydrogenation takes place. As soon, however, as a sufficiently high temperature is reached, Erdmann thinks these organic nickel salts, under the influence of hydrogen, are decomposed in such a way as to form nickel oxide and the suboxide, which latter possesses the property of forming an oil colloid and becomes active as a catalyst.

Under some circumstances a mirror of metallic nickel forms on the walls of the vessel; this occurs especially easily when nickel oleate is used, and also has been noted with nickel formate when the oil is maintained at a relatively high temperature, approximately 250° C. The metallic nickel which forms as a mirror or otherwise, it is claimed, does not exert a catalytic action, but the nickel oxides which arise and which pass into the oil in a finely-divided condition are effective catalysts.*

The application of organic nickel salts, such as nickel formate, suffers the disadvantage that the action is not immediate, because time is required to effect the decomposition of the formate. Furthermore, there is the loss in formic acid and the costliness of regenerating the catalyzer.*

* Bohm (Seifen. Ztg. (1912), 737, Soap Gazette and Perfumer, 1913, 107) advances the rather sweeping view that many of the patents issued subsequent to the Leprince and Siveke German Patent 141,029, 1902, have little or no standing. He states that operations involving changes in air pressure are common expedients of organic chemistry; that spraying oils to secure intimate contact with gases is well known, citing such use in the linseed oil industry; and that metallic catalyzers in the colloidal form may fall within the definition of a finely-divided metal. He, however, regards the metal *salt* catalyzers as being independent of the Leprince and Siveke Patent, but expresses some doubt as to the continuance of their use in Germany after the expiration in 1917 of German Patent 141,029.

The views of Bohm are criticized in the Seifensieder Zeitung (1912), 1001, his idea that almost all patents for oil hardening will lose their value with the expiration of the Leprince and Siveke Patent in 1917 being regarded as erroneous. The contrary is more likely to take place, that is, the value of these processes will advance. It is a matter of surprise that Bohm regards the metal salt catalyzers as independent of the Leprince and Siveke Patent. Nickel formate, as well as other salts, such as

Sabatier and **Espil** have studied the reduction by hydrogen of nickel oxide obtained by igniting the nitrate. Reduction takes place at 170° C., at which temperature, after 112 hours, 72 per cent were reduced. Thereafter the reaction progressed more slowly and after 160 hours the conversion amounted only to 80 per cent. These and other observations appear to disprove the claim made by Glaser that below 330° C. not over 50 per cent of nickel are reduced and that the oxide Ni_2O is produced. In fact, the work of Sabatier and Espil would indicate the existence of a difficultly oxidizable oxide having the formula Ni_4O.*

Sabatier and Espil in a further investigation of the question of degree of reduction of nickel oxide when heated in the presence of hydrogen make note † that a careful calcination of nickel nitrate affords nickel oxide which reduces to metallic nickel at a temperature of 155° C. without the production of a non-reducible suboxide. When the oxide is calcined at a bright red heat reduction takes place at 155° C., but the action is slower.

An additional contribution to this subject by Sabatier and Espil (Comp. rend. 1914, 668) indicates that sufficient metallic nickel is formed from the oxide in oil to explain the catalysis observed in the case of the Bedford-Erdmann process. Sabatier and Espil use the term *coefficient of reduction* to represent the proportion of oxide reduced per hundred parts. At 240° C. on three hours exposure to hydrogen, an oxide of nickel which had been prepared by calcination at 550° C.

nickel lactate, acetate, etc., proposed by Wimmer and Higgins, are first broken down into nickel oxide and acid; while under the influence of heat and hydrogen the organic acid is further decomposed and the nickel oxide, at least in part, apparently is reduced to metallic nickel. Without the presence of metallic nickel hydrogenation is thought to be scarcely possible.

The decomposition of nickel formate into acid and metallic nickel is said to be very easily demonstrated by a laboratory test. Wimmer and Higgins may perhaps conduct the process so as not to form metallic nickel. A serious disadvantage exists in the regeneration of the once-used contact material of this character; for reconversion into nickel formate, acetate and other costly organic salts is an expensive operation. The oxide catalyzers likewise would be expected to form metallic nickel during the hydrogenation process, even though the reduction be only partial. From the work of Ipatiew such reduction apparently does not take place. Possibly the envelopment of the molecules of oxide by oil hinders the reducing action of the hydrogen.

The doubts formerly had with regard to the effectiveness of oxide catalysts have now vanished, for during a considerable period this contact material has been used for hardening oils on the large scale. A reduction of the oxides to the metallic state has not been observed under these circumstances.

* Chem. Ztg. (1913), 1121.

† Chem. Ztg. (1913), 1549.

showed a coefficient of reduction of 93, while oxide which had been ignited at a bright red heat exhibited a coefficient of 32.8. (These figures relate to the dry oxide not in oil.) At 155° C. on 96 hours exposure to hydrogen, a light oxide gave a reduction coefficient of 56 and a calcined oxide was found to have a coefficient of only 2.5. The rate of reduction was found to be somewhat accelerated by increase in the rate of flow of hydrogen over the oxide mass. At 240° C., with a rate of flow of hydrogen of 6 cu. cm. per minute the coefficient was 44.5, at 17 cu. cm. the coefficient increased to 65 and at 24 cu. cm. the coefficient became 77.5. Sabatier and Espil note that elevation of the temperature greatly increases the speed of reduction. At 220° C. with oxide of nickel, the following coefficients were obtained.

1 hour	14.9
4 hours	57.6
5.5 hours	77.4
6.5 hours	78.0
7.5 hours	79.9
22 hours	99.6

At 250° C. the coefficients were found to be as follows:

½ hour	30.0
1 hour	52.0
1.5 hours	78.9
2 hours	87.0
2.5 hours	92.5
3 hours	95.3
15 hours	100.0

Between 190° to 240° C. the speed of reduction is an exponential function of the temperature. The reduction of nickel oxide at 175° C. gave a coefficient of 10 and on treating this product with carbon monoxide at 50° C. nickel carbonyl was obtained. Sabatier and Espil conclude that a suboxide is formed by reduction in this manner, having the composition Ni_4O, corresponding to the coefficient 75. This suboxide is not, however, irreducible but is, as stated above, more slowly reduced than the protoxide.

Dry hydrogen has been found to reduce the oxide better than moist gas and in practice it is recommended that the hydrogen employed for reduction purposes be freed from moisture before use.*

† Sabatier and Espil have observed that moist hydrogen is at least as active as dry hydrogen in the hydrogenation of benzene and phenol (Bull. Soc. Chim., 1914, 228).

The rate of hardening of cottonseed oil by nickel and nickel oxide catalyzers has been investigated by **Meigen** and **Bartels** (J. prakt. Chem., 1914, 293) and their results are shown in Fig. 43. Curves 1, 2 and 3 were derived with metallic nickel at 170° C., and 4 and 5 with nickel oxide at 250° to 255° C. The amount of catalyzer in all cases corresponded to two per cent of nickel oxide. No. 1 was obtained with nickel prepared from the carbonate, No. 2 from reduced oxide and No. 3 from a commercially-used catalyzer. The oxide employed in Nos. 4 and 5 was obtained by ignition of the nitrate. These curves indicate a slower action for the oxide, which Meigen and Bartels attribute to the time required for preliminary reduction of the oxide after its addition to the oil, and before actual hydrogenation of the oil occurs.

Free oleic acid can be hardened very easily by means of a nickel oxide catalyzer, according to *Bedford* and *Erdmann.** Nickel oleate forms only in slight amount.

Pure nickel, obtained by reduction of the nitrate, according to Chem. Fabr. auf Actien,† is inactive for the purpose of converting borneol into camphor; if, however, a small quantity of sodium carbonate be added to the nitrate before reduction, a very active product is obtained; a similar mixture is obtained by adding 0.17 per cent of pure sodium oxide to the nickel; other bases or salts which are not readily reduced at a red heat may be used in place of sodium oxide. Further, if a small quantity of certain other metals is introduced into the nickel, the mixture will have a very powerful catalytic action. Mixtures of 6.7 per cent of cobalt or copper with 93.3 per cent of nickel may be used; they are obtained by the reduction of the mixed nitrates. The process is not confined to the use of nickel; it is stated that other metals possessing catalytic action can be used with equal effect.

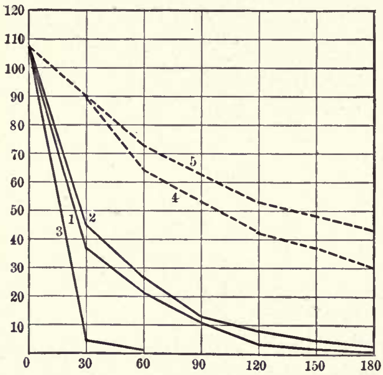


Fig. 43.

By a method somewhat similar to that of Bedford and Erdmann the proposal comes from **Kast** ‡ to prepare catalysts in a finely-divided volu-

* Jour. f. prakt. Chem., 1913, 450.

† French Patent 401,876, April 8, 1909; German Patents 219,043 and 219,044, 1908.

‡ U. S. Patent 1,070,138, Aug. 12, 1912.

minous condition by heating the trinitrophenol salt of a heavy metal. These salts are combustible and when ignited they expand greatly, so the resulting ashes (metal or metal oxide) are found to be in a voluminous, spongy form. Kast claims that the usual procedure of precipitating a salt solution (with or without a carrier) yields a coarse crystalline precipitate, and that reduction by heating in a reducing gas slags the precipitate in consequence of which the catalytic effectiveness is considerably diminished. To avoid danger of an explosion when decomposing the trinitrophenol compound by ignition Kast adds oil or tar as a diluent. He also recommends for this purpose nitrate of ammonia, as this salt evolves large quantities of gas on heating and leaves no residue. The formation of slag which Kast objects to in ordinary reduction seemingly would be aggravated when a salt of trinitrophenol is burned under these conditions.

The hydrogenation of unsaturated fatty acids and their esters may be effected, according to **deKadt,*** by means of hydrogen in the presence of a catalyst consisting of a soap of a heavy metal or of a noble metal, made from a fat or fatty acid having a melting point higher than that of the saturated compound to be produced. For example, the nickel soap, or preferably a mixture of the nickel and iron or copper soaps of the fatty acids of stearine or Japan wax, is dried and powdered, and can then be intimately mixed with the oil to be hydrogenated. After hydrogenation the oil is left quiescent at a temperature above its melting point, when the soap particles will agglomerate and settle on cooling. If, however, the oil is kept in motion and filtered, the soap does not pass through the filter. It is stated that this process is more efficient than when metallic catalysts are used, owing to the more intimate contact between the catalyst and oil or fat which is here obtained.

Basic compounds of high molecular fatty acids with certain of the heavy metals are proposed as catalyzer formative material by **Hausamann.**† The compounds dissolve in the oil undergoing treatment and in the presence of hydrogen afford active catalytic bodies. The temperatures employed range from 100° to 180° C. After the oil has been hardened it may be treated with dilute acid to remove the catalyzer.‡

The employment of a basic salt of a heavy metal (nickel or copper) with a fatty acid is recommended by *De Nordiske Fabriker De-No-Fa Aktieselskap* as a catalytic material in the hardening of fats or fatty

* British Patent 18,310, Aug. 9, 1912.
† Zeitsch. f. angew. Chem. (1914), 63, No. 7.
‡ See also Seifen. Ztg. (1914), 7.

acids. About 0.4 per cent of the metallic compound is used and the hydrogenation takes place at temperatures between 100° C. and 180° C.*

Organic compounds of metals, such as metallic salts of organic acids, are employed by **Wimmer** and **Higgins** † as catalytic agents in the reduction or hydrogenation of various organic compounds; thus the copper, iron, nickel or cobalt salts of formic, acetic or lactic acid may be employed. The advantage of these compounds is that they can readily be mixed with the compound to be reduced, either in the form of a solution or as an "emulsion"; thus the compound may be emulsified with the catalyst and at the same time treated with hydrogen. It is stated that hydrogenation may be accelerated either by using the hydrogen under pressure, or by impregnating the compound to be reduced with hydrogen, and then bringing it into intimate contact with the catalyst. One detailed example is given in the specification, describing the treatment of 100 grams of cottonseed oil with hydrogen in presence of 1 to 5 grams of nickel formate at a temperature of 170° to 200° C.

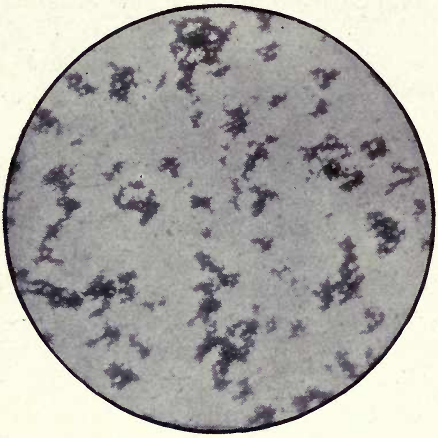


Fig. 44. — Photo-micrograph of nickel precipitated in cottonseed oil by the action of hydrogen on nickel resinate dissolved in the oil. × 100.

Wimmer makes the statement that these organic salts are not reduced to the metallic condition during hydrogenation.‡

Bedford and **Erdmann** § state that nickel formate yields nickel suboxide at 210° C., while metallic nickel is formed at 250° C., and that nickel acetate, oleate and linoleate behave in a similar manner.

Higgins ‖ uses nickel or zinc formate in the reduction of organic compounds without the application of gaseous hydrogen.

Several other methods of producing catalyzers have been the sub-

* J. S. C. I., 1914, 324.
† French Patent 441,097, March 8, 1912.
‡ Seifen. Ztg. (1913), 1301.
§ Zeitsch. f. ang. Chem. ref. (1913), 751.
‖ Chem. Ztg. Rep. (1913), 680; British Patent 23,377, Oct. 12, 1912.

ject of the patents as, for example, that to **Crosfield** * in accordance with which kieselguhr and the like is impregnated with a solution of nickel sulfate and the impregnated material treated with alkali hydrate to precipitate nickel hydrate in and on the porous material. The product is then well washed, dried and reduced. If kieselguhr is used the powder should contain about 30 per cent of metallic nickel.†

A similar procedure is the subject of a patent to **Kayser.**‡ In this case, however, the nickel sulfate or other nickel salt in concentrated solution may be used in an amount to saturate kieselguhr while leaving it in an apparently dry condition, when it is incorporated with a molecular proportion of powdered carbonate of soda and the mixture thrown into boiling water, dried and reduced.

Kayser states that there are various known ways for producing metallic powders in a state of fine division. Nickel powder, which for many purposes is recognized as the most potent catalyzer technically available, is, for example, most conveniently produced by acting upon such nickel compounds as the chloride, oxide, hydrate or carbonate at an adequate temperature with hydrogen. The catalytic energy of such a powder, however carefully prepared, he says, is at best an uncertain quantity; frequently it is feeble, as sometimes, for no conclusive reason, it is altogether lacking. Furthermore, powder thus produced is specifically heavy and he claims cannot be easily kept in suspension in a liquid medium like oil, when that is desired, nor can it, since it forms an almost impervious sediment, be readily separated and recovered from such liquid medium by a contrivance like the filter press. The same objections, he says, apply to nickel powder prepared by other means; and, in the endeavor to improve on these, Kayser brings a compound of nickel, such as the nitrate, oxide, hydrate or carbonate, into intimate contact with an inert, absorptive and comparatively bulky mineral substance, such as kieselguhr and infusorial earth, dries and comminutes the product, and reduces the powder thus produced. In one case he saturates kieselguhr with a solution of nickel nitrate, dries the mixture, employing in the case of the nitrate sufficient heat to expel the nitric acid, grinds the resulting product and reduces with hydrogen. Another way is to permeate or saturate kieselguhr with a solution of nickel chloride, nickel sulfate or other soluble nickel salt, enter the resulting product, with or without previous drying, into a boiling solution of carbonate or hydrate of soda or other suitable precipitant, remove the soluble salts, formed by washing, dry and comminute the residue, and reduce it as before. A third and preferred method, as stated, is to saturate the kieselguhr with a solution of nickel chloride, nickel sulfate or other nickel salt, using so much solution only as will leave the kieselguhr in an apparently dry and freely workable

* British Patent 30,282, 1910.

† Ubbelodhe and Woronin (Petroleum (1911), **7**, 9) prepared a catalyzer by crushing a plate of porous clay (which had been ignited) to form particles of about the size of peas. Nickel nitrate was melted and heated until water vapor ceased to be evolved. Then the clay particles were added and the mass was stirred and strongly heated to expel the oxides of nitrogen. This step was followed by reduction with hydrogen at 360° C.

‡ U. S. Patent 1,004,034, Sept. 26, 1911.

condition, incorporate a molecular proportion of powdered carbonate of soda or other powdered precipitant, throw the mixture with constant stirring into boiling water, remove the soluble salts formed by washing, dry and comminute the mixture, and reduce as before.

To develop the highest catalytic efficiency, Kayser states that the kieselguhr should become evenly and completely coated and permeated, plated as it were with a film of metal, and that a catalyzer composed of one to two parts by weight of metallic nickel and four parts by weight of kieselguhr has however proved very effective in saturating fats and oils by means of hydrogen. The author can see no advantage in permeating or impregnating the interior canals of the carrier with catalytic metal when the catalyst is to be used for hydrogenating fatty oils. The porous support used by Sabatier and Senderens, to be sure, was impregnated with reduced nickel, but these investigators directed their attention to the hydrogenation of readily volatile substances, capable of diffusing into the interior of the nickel-laden porous material.

Seeking to overcome the disadvantage of ready oxidation in the air possessed by normal catalytic nickel, Kayser * reduces the nickel oxide or equivalent material at a temperature of 500° to 600° C. and then passes through the reduced material a brisk current of carbonic acid until the escaping gas proves no longer inflammable. By this method it is claimed that a catalyzer is secured which will remain perfectly cool on exposure to the air and even may be exposed for days without losing any of its catalytic energy, a result which probably is due to elimination of occluded hydrogen.†

Wilbuschewitch ‡ proposes to secure more rapid reduction of catalyzer by agitating it in the presence of hydrogen in a heated rotary drum. The temperature during the treatment is stated to be 500° C. Wilbuschewitch § has patented a process of regenerating spent catalysts of the nickel type, involving extraction with benzene, treating with alkali solution, acidifying, treating with sodium carbonate solution and reducing.

The recovery of catalytic material is described by Naamlooze Vennootschap, Ant. Jurgen's Vereenigde Fabrieken in British Patent 27,233, 1913.‖ The catalyzer is freed from organic matter by heating in a current of air, the material is treated with an acid to dissolve metal from its insoluble carrier and the metal is then precipitated on the same carrier.

* U. S. Patent 1,001,279, Aug. 22, 1911.

† The Bremen-Besigheimer Olfabriken (Seifen. Ztg. (1913), 1007) recommend the exposure of catalytic material to an atmosphere of carbon dioxide, or inert gases. The catalyzers produced in this manner are stated to be permanent and to possess great activity.

‡ U. S. Patent 1,016,864, Feb. 6, 1912.

§ U. S. Patent 1,022,347, April 2, 1912.

‖ Seifen. Ztg. (1914), 169.

Bedford and **Erdmann** * treated a quantity of used nickel oxide catalyzer with dilute sulfuric acid. Hydrogen, accompanied by hydrocarbons of disagreeable odor, was evolved. A carbonaceous residue amounting to 6 or 7 per cent remained after treatment with the acid. Nickel oxide has been found to take up silica when used repeatedly as a catalyzer. The same absorption of silica also occurs with palladium.

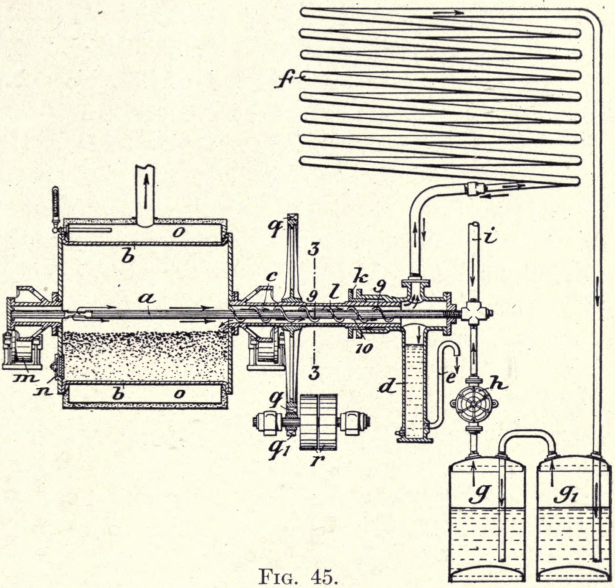


FIG. 45.

Wilbuschewitsch, in U. S. Patent 1,029,901, of June 18, 1912, describes a process of making a catalyst in which he takes, for example, nickel sulfate in the form of a solution of strength of 10 to 14 degrees Baumé, mixing this with about double its weight of an inorganic substance such as clay, asbestos, pumice stone, kieselguhr or the like, from which all soluble matter has been removed by treatment with an acid. The mixture is then treated with carbonate of soda to convert the metal salt into a carbonate. The composition is heated to about 500° C. so as to transform the carbonate into the oxide. Reduction with hydrogen is then carried out and the product is ground with oil until, as the patentee states, a strongly viscous liquid, similar in character to an emulsion, is produced.

An apparatus employed by Wilbuschewitsch,† Fig. 45, for the re-

* Jour. f. prakt. Chem., 1913, 444.

† U. S. Patent 1,029,901, June 18, 1912.

duction of nickel compounds consists of a cylindrical drum *b* mounted to rotate on rollers *m* and provided with a heating jacket *o*. The material is charged into the drum through an inlet opening *n*. To one of the end plates of the drum a tubular shaft *c* is secured which, with its free end, is guided in a stuffing box *k* supported in a lateral stud of a tubular receptacle *d*. On the shaft a spur gear *q* is mounted which is in mesh with a pinion q_1 adapted to be rotated by means of a belt pulley *r*. By means of the gearing q', *q* the drum *b* is slowly rotated, and during such rotation it is heated to about 500° C. Hydrogen is then forced into the drum through a pipe *a* located coaxially within the hollow shaft *c* and connected at one end to a tube *i*. The hydrogen is passed through the material to be reduced, and from the latter it is successively conducted through an automatically operating dust collector 9 connected to the retort, a cooling worm *f* and purifying vessels *g*, g' containing respectively acid and caustic soda lye, or a similar purifying medium. After thus being regenerated it is returned by means of a pump *h*. The water produced by the reduction is condensed in the coil *f* and is dropped from the coil *f* into the vessel *d* from which it is withdrawn through an overflow *e*. The dust collector 9 by means of which the hydrogen escaping from the drum is prevented from carrying along particles of dust is constructed in the form of a worm conveyor *l*. The dust moves through the hollow shaft *c* in the direction of the gas flow and owing to the difference in the speed of the gas and dust the latter is deposited on the bottom of the shaft *c*, and is conveyed back into the retort by the worm *l*.

A procedure noted in connection with Crosfields & Sons, Ltd., vs. Techno-Chemical Laboratories, Ltd.,* disclosed as apparatus a cylindrical autoclave 1 meter high and $\frac{3}{4}$ meter in diameter (inside measurements), with a steam jacket, and fitted with a non-conducting lining of unknown material. Nine kilograms of cotton oil were pumped into the autoclave, and 288 grams of a composition, containing a catalytic agent, were used and were mixed with the oil prior to the introduction of the mixture into the autoclave. The autoclave was then filled with hydrogen from a cylinder to a pressure of 15 atmospheres. During the operation the pressure varied from time to time according to the absorption of hydrogen. A mechanically driven circulation pump was connected with the autoclave both by its suction and delivery conduits. By means of a pump and a jet for spraying, a mixture of oil and composition containing the catalytic agent was drawn from, and forced back into, the autoclave. The iodine absorption was not determined. The composition containing

* British Official Journal Supplement, June 18, 1913, 301.

the catalytic agent was prepared from a salt of nickel. The catalyst employed was prepared as follows: About $1\frac{1}{2}$ kilograms of nickel sulfate were dissolved in 3 liters of water, and the same weight of sodium carbonate, dissolved in the same quantity of water, and at about 70° to 80° C. was added to the nickel sulfate, which was at 60° to 70° C. The mixture was stirred for $1\frac{1}{2}$ to 2 hours, and the precipitate was filtered off and washed with distilled water at about 25° C. for 60 to 70 hours alternately in tanks and filter press. A small sample was dried and tested to ascertain that the precipitate had been sufficiently washed. The washed precipitate was dried in hot air at 80° to 85° C., and was calculated to weigh 720 grams. It was then roasted in a pan for about 15 minutes over an open Bunsen gas burner, and the weight after roasting was calculated to be about 380 grams. The product was heated to about 300° C. for about 6 minutes in a current of hydrogen in revolving glass tubes slightly inclined, the precipitate being introduced at the higher end and through a spiral glass tube, and the hydrogen at the lower end. The product, which weighed 288 grams, was directly introduced into a small quantity of oil, which was mixed with the 9 kilos the following day.

Catalyzers said to possess high activity are produced by mixing with oil a base-metal compound of an easily-reducible character and yielding the catalytic metal on reduction, heating and bringing a reducing gas under pressure into contact with this mixture.*

Nickel carbonyl is employed by **Franck** † to form catalytic material by precipitation of nickel from the carbonyl in an oil menstruum in the presence of solid material. The latter may be kieselguhr or nickel or copper oxides or reducible metallic salts. The solid material is heated with the oil and nickel carbonyl conducted into the mixture.

Eldred ‡ does not regard a finely-divided catalyst as desirable as one having a catalytic metal welded to a heat-conducting support. He states that since the amount of such catalytic action performed in a given time unit in a body of gas is strictly proportionate to the exposed surface of catalyzing metal, it is customary to use such metals in finely-divided form, sometimes as masses of powder and sometimes as powders adhering to and held by inert porous materials, such as asbestos, glass wool and the like, but that these expedients while giving great surface to a given amount of metal do not give a proportionately great exposure of such metal to the gases or vapors to be treated. It is substantially impossible to drive or distribute gases

* Seifen. Ztg., 1913, 1298.

† Seifen. Ztg., 1913, 1271.

‡ U. S. Patent 1,043,580, Nov. 5, 1912.

uniformly throughout a body of powder, and in passing gases over a body of such powder it is substantially only the top layers of the powder which display a maximum activity, underlaying layers not functioning to any great extent. Use of very thin layers of powder of course necessitates unduly extended shelf surface. Eldred observes that nearly all catalyses are exothermic reactions, heat being developed by the action, and frequently the amount of heat is rather large. And as it is usually desirable to work within comparatively narrow temperature limits, keeping and maintaining the catalytic metal within a few degrees of some definite temperature, this evolution of heat may become a serious matter. Nearly all the catalytically acting metals in the form of powders are relatively poor conductors of heat. When, for example, platinum is distributed through a mass of such a heat insulator as asbestos, it is very hard to prevent the accumulation of reaction heat in the metal. Hence Eldred proposes a catalytic body comprising the catalytic metal in the form of a very thin continuous layer or film supported by masses of better heat-conducting metals weld-united to such layer or film and therefore in absolute metallic union therewith so that by controlling the temperature of the carrying metal the temperature of the film or layer can also be controlled. A catalyst may be made by welding a sheath or coating of platinum on a billet of copper or steel and "coextending" the joined metals to form wire or sheet metal. If 3 to 10 per cent of platinum be placed on the original billet and coextension be performed with care, the wire, sheet or leaf metal formed will also have 3 to 10 per cent of platinum, but this thickness in such coextended ware will correspond to an extremely tenuous layer. Cobalt and nickel may be united to steel or copper billets, and the duplex or compound billets extended in similar manner to produce catalysts having film coatings of cobalt or nickel. The cobalt or nickel may be united to the underlying core metal directly or through a linking layer of another metal such as gold, silver or copper. Eldred mentions the cobalt and nickel catalyzers as useful in hydrogenation reactions.

In the preparation of a catalytic body **Ellis** * recommends the use of wood charcoal which possesses the property of absorbing or occluding hydrogen and when incorporated with nickel or other metal catalyst serves as an activator and storehouse of hydrogen. If nickel is used, a ratio of one part of metal to four parts of charcoal is best not exceeded. The metallic compound may be precipitated more or less on the surface of the charcoal particles by wetting the latter with a solution of a precipitant and adding a solution of a nickel salt. Pre-

* U. S. Patent 1,060,673, of May 6, 1913.

cipitation under these conditions is largely external. Exposure of the composition to the air after reduction is to be avoided.*

Müller † finds the catalytic activity of iron and nickel, especially in connection with processes for the introduction of hydrogen into glycerides of unsaturated fatty acids, is considerably augmented and caused to resemble in activity the catalytic properties of the noble metals, such as palladium, if the former metals after ignition in hydrogen are heated in a stream of carbonic acid gas in order, apparently, to destroy the metal hydrides which are formed and convert the catalyzer into the pure metal. Müller says the process also makes possible the elimination of finely-divided catalyzer, whose production and application the patentee states is accompanied with many difficulties, and its replacement by coarse fragments of metal, such as filings and shavings of iron, nickel and copper, first igniting the latter in hydrogen and then in carbonic acid gas. He states that common iron filings caused a reduction of the iodine number of only 2½ per cent in two hours, while using filings which had been treated with carbon dioxide the iodine number was reduced 25 per cent.

When nickel hypophosphite solution is boiled, metallic nickel is precipitated, under some conditions as thin metallic leaves; under other conditions as a fine powder. The latter form acts catalytically on sodium hypophosphite in solution giving acid sodium phosphite with evolution of hydrogen. The powder form is obtained by dissolving 20 grams nickel sulfate in 100 cc. water, heating on a water bath, introducing in one addition 70 grams sodium hypophosphite and stirring. At the end of one hour reduction is complete. Distilled water is added, the nickel material is allowed to settle and is washed by decantation.‡ Palladium prepared in a somewhat similar manner decomposes sodium hypophosphite very effectively.§

On account of the relatively low degree of sensitiveness of nickel oxide catalyzers to the usual catalyzer poisons **Erdmann** ‖ was able to readily hydrogenate Japanese fish oil containing a high content of free fatty acid and also certain sulfur-containing oils, such as Egyptian cottonseed oil.

If the hardening operation is interrupted before the reaction is com-

* See also Ellis, U. S. Patent 1,088,673, Feb. 24, 1914.

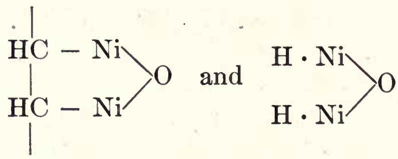
† Seifen. Ztg. (1913), 747; French Patent 540,703 (1912); British Patent 22,092, Sept. 28, 1912, to Müller Speisefettfabrik.

‡ The author has noted that this precipitated nickel material is catalytic and readily acts to harden cottonseed oil at a temperature of 210° C., or thereabouts, with hydrogen at atmospheric pressure.

§ Breteau, Bull. Soc. Chim. (1911), 9, 515–519.

‖ Chem. Ztg., 1913, 1142, 1173 and 1195.

plete, and the catalyzer collected by centrifuging, extraction with benzol or other solvents shows the rate of removal of the residual fatty substances from the catalyzer to be very slow. The fat clings strongly to the catalytic body. On the contrary when the reaction is at an end the catalyzer separates in a flocculent condition. Because of this, Erdmann is of the opinion that the oxide and unsaturated fat form a loose addition compound which is subsequently split by hydrogen. Analysis of the black nickel material obtained by extracting the fat from used catalyzer shows several per cent of carbon to be present, apparently united to the nickel as a kind of carbide. The greater portion of the used catalyzer consists of a mixture of nickel oxide and suboxide. The latter is looked upon as Ni_2O, described by Bellucci and Corelli.* The hydrogen transference probably takes place in one of two ways: either an intermediate phase represented by the compounds



is formed (the latter compound carrying its hydrogen very loosely bound); or a decomposition of water may take place in accordance with the reaction

$$Ni_2O + H_2O = 2\,NiO + H_2$$

yielding hydrogen in a nascent state which is assumed to unite with the unsaturated fat, while the nickel oxide formed is reduced to the suboxide by hydrogen in the molecular condition. Which of these views is correct can be ascertained only by further investigations. Hydrated nickel oxide or nickel carbonate may be used in place of the oxide, and under some conditions apparently also nickel salts such as the formate and acetate. These salts act as hydrogen carriers only after the acid radical has been split up and the free metallic oxide formed.

The conclusion is reached by **Bedford** and **Erdmann** † that some of the organic salts of nickel act like nickel oxide as catalyzers and form in fact nickel oxide by decomposition when heated in the presence of hydrogen. A number of tests were carried out using nickel formate, acetate, oleate and linoleate. In one case 200 grams of cottonseed oil were heated to 253° C. with nickel formate (equivalent to 2.4 grams

* Atti. R. Accad. dei Lincei, **22**, I, 603 and 703.

† Jour. f. prakt. Chemie, 1913, 449.

NiO), and hydrogen passed into the mixture. The oil quickly darkened due to the formation of finely-divided nickel and nickel oxide. After one and one-half hours the solidifying point of the fatty product was 51.2° C. 200 grams of cottonseed oil, 6 grams of nickel acetate and 20 cc. of water were heated and hydrogen passed therethrough. The temperature was brought to 215 to 220 degrees. The acetate retained its green color unchanged and no hardening of the oil was observed. The temperature was then raised to 240 to 250 degrees when the mixture turned black and in one and one-half hours the solidifying point of the hardened oil was 49 degrees. 250 cc. linseed oil with 6.3 grams of nickel linoleate (equivalent to 1.2 gram NiO) was treated with hydrogen at 2.65 degrees for three hours yielding a product having a solidifying point of 44.5° C. The catalyzer at the close of the test consisted of nickel oxide and suboxide and nickel soap. Using 11.5 grams of nickel oleate to 200 grams of cottonseed oil it was found that the black coloration occurred above 220 degrees. Hydrogenation was carried on at 250 degrees and after two hours the solidifying point was 41 degrees. On the glass walls of the reaction flask a brilliant mirror of metallic nickel formed, which in the course of time separated in coarse flakes.

A catalyzer which remains easily in suspension is prepared according to the **Bremen-Besigheimer Ölfabriken** * by incorporating a metal salt with an inorganic carrier and drying this product in the presence of the unsaturated material which is subsequently to be hydrogenated, or for that matter with any suitable indifferent liquid. The mixture is treated so as to expel all of the water and a part of the volatile acid of the salt which otherwise might become free and act injuriously during the reduction process.

By this removal of water and acid the catalyzer is put into such a condition that it is capable of remaining suspended in oils and fats. In the application of the catalyzer for the reduction of the latter a carrier, such as kieselguhr, asbestos and the like, is treated with a solution of a metallic salt, such, for example, as nickel acetate. After drying the material it is ground with a quantity of oil so as to yield the catalyzer in an extremely finely-divided condition and disseminated through the oil vehicle. The water and acetic acid are now removed by heating the mixture to 150° to 200° C. in a closed vessel fitted with an agitator and vacuum pump. After the volatile material has been removed by such a treatment, hydrogen is conducted through the resulting product.†

* Zeitsch. f. angew. Chem. (1913), Ref. 604.

† A form of treatment of oil and catalyzer with hydrogen, as disclosed by the Besigheimer Ölfabriken, is noted in Seifen. Ztg. (1913), 1007.

Higgins * states that the conversion of unsaturated fatty acids or their glycerides or other unsaturated compounds into the corresponding saturated compounds, by means of hydrogen in presence of finely-divided nickel or other metal, is accelerated by the presence of formic acid or other volatile organic acid. From 1 to 2 per cent of formic acid, calculated on the weight of unsaturated material, has been found a suitable proportion. The hydrogen may be passed through a vessel containing the volatile acid before admitting it to the mixture of unsaturated compound and metal.

According to **Wimmer** and **Higgins** † catalytic material may be prepared from nickel salts, such as nickel formate, by mixing with a protecting material, the latter, for example, being an oily body, and then reducing the salt to yield the nickel in a metallic condition. The oil serves to preserve the catalytic properties of the reduced substance.

Wimmer has observed that the content of free fatty acid is increased by hydrogenation and has offered as a remedy the addition of drying agents to the catalytic material. Ignited sodium or magnesium sulfate are recommended for the purpose. In hardening cottonseed oil Wimmer uses 3 to 10 per cent of sodium sulfate and 2 to 3 per cent of nickel formate calculated on the weight of the oil. He found a sample of peanut oil containing 0.5 per cent of fatty acid, after hardening in this manner, to contain 0.42 per cent of fatty acid, while without an addition of sodium sulfate the acid content was 0.72 per cent.‡

A flaky form of nickel catalyzer is brought forward by **Hagemann** and **Baskerville** § to replace nickel supported on an inert carrier. They observe that the application of the latter type of catalyzers involves a number of technical difficulties; for instance, on account of their finely-divided state, such catalyzers cannot be readily and satisfactorily separated and recovered from the fats, and, owing to their density, do not remain well suspended in the oil treated, when such suspension is desired. The use of a metal precipitated upon an inert carrier, such as kieselguhr, they note, has not given entirely

* British Patent 18,282, Aug. 8, 1912.

† French Patent 454,501, Feb. 18, 1913. When nickel formate is used, it serves both as reducing agent and as catalyst; with zinc formate, addition of a known catalyst, such as palladium chloride, is desirable. The temperature used is preferably about 20° C. below that at which the formate would decompose into the oxalate at the pressure existing during the operation. (Higgins, British Patent 23,377, Oct. 12, 1912.) Wimmer and Higgins (Seifen. Ztg., 1914, 7) state that the metal salts of organic acids may be used for the hydrogenation of various organic compounds of an unsaturated nature in addition to oils and fats.

‡ Seifen. Ztg., 1914, 390.

§ U. S. Patent 1,083,930, Jan. 13, 1914.

satisfactory results, probably for the reason that only a small part (one side) of the film of the precipitated metal comes into actual contact with the liquid to be reduced and the hydrogen, and the remainder of the metal is consequently inactive, since the reacting materials cannot come into contact therewith. Other stated objections to the use of such a catalyst are that the process of revivification is quite an expensive undertaking, since the metal must be dissolved in an acid, and reprecipitated upon kieselguhr; that it is difficult to obtain a catalyzer by precipitation and reduction methods, which is free from oxides and other impurities; and that fatty oils hydrogenated with such finely-divided catalyzers will contain metallic soaps, such as soaps having a nickel base, which are undesirable from economic and hygienic standpoints. Hagemann and Baskerville observe that metals having catalytic activity, such as nickel, or cobalt, brought into a state of extremely thin films, or flakes, by mechanical, chemical or galvanoplastic processes, as, for example, by the method shown by Edison,* offer technical advantages as catalysts in the hydrogenation of fatty oils. These films, or flakes, are obtainable in a state of high purity, and may be employed either in the metallic (pure) state or after being partially oxidized. Films can readily be prepared, having a thickness of from one twenty-thousandth to one forty-thousandth of an inch, and accordingly the efficiency of a given weight of a catalytic metal, for example, nickel, when applied in this form, is high, owing to the large amount of exposed surface. Such films, or flakes, will, on account of their extreme thinness, readily float and remain evenly distributed throughout the whole mass of fats or oils.† The separation of the hardened products from the flaky nickel, cobalt, etc., is said to be accomplished without difficulty. In the revivification and recovery of the catalyzer for subsequent use it has been found that flaky metals, as nickel, etc., admit of economical treatment, for the flakes retain their physical form. In this revivification the flakes, or films, from which the fat has been removed (for example, by extraction with a suitable solvent) are subjected to superficial oxidation followed by reduction with hydrogen at, say, 300° C., or higher, in a current of oxygen or air, or by treatment with oxidizing agents in liquids in which the metallic flakes are suspended. In such a manner Hagemann and Baskerville state they can repeatedly produce freshly-reduced surfaces to both sides of the metal flakes, or films, without

* U. S. Patent 865,688. See also 821,626.

† The author has made use of a form of flaky nickel derived from nickel carbonyl in hydrogenating oils and has found this form of the metal to be satisfactory from the catalytic standpoint.

having recourse to conversion of the metal into a soluble salt, precipitating, igniting and reducing.

Another method* of forming a catalyzer involves the utilization of the disintegrating effect of an electrical current or arc between a pole or poles of nickel immersed in a vehicle offering considerable resistance to the electric current, such as water, or aqueous solutions, thereby producing nickel material in a finely-divided condition, requiring little or no further treatment to serve as a catalyzer. For example, two electrodes of pure nickel in bar or rod form are connected one to the positive and the other to the negative pole of a source of electricity. The ends of the nickel rods are dipped in water and brought in contact, then separated so as to form an arc under the water. This results in the production of nickel material usually of a brown to blackish color in a state of more or less fine division, some of this material often being so fine and flocculent as to remain suspended in water for several days. Distilled water should preferably be used though under some circumstances saline solutions may be employed. By the use of distilled water the introduction of contaminating bodies is practically or entirely avoided.

Careful regulation of the arc is desirable in order to avoid melting away particles of nickel in the shape of large fragments which are not useful for the present purpose, although some coarse material is usually formed. When the product contains such heavy nickel particles it may be levigated and the lighter sludge separated from the heavy nickel residue. The sludge is evaporated to dryness when a very light nickel material is obtained, which may be used at once as a catalytic body or may first be reduced in hydrogen. Or, the wet sludge may be heated with oil to expel the water in order to produce a form of nickel which remains suspended in oil for a long period and this may be used as catalytic basis. In such a case it is usually well to heat to 230 to 250° C. in the early stage of the hydrogenation treatment and after a time the temperature may be reduced to 200 degrees and lower.

Boberg † prepares a catalyst by reduction with hydrogen of a metallic compound, such as ignited nickel carbonate, under such conditions that the resulting product is a complex compound of one or more suboxides of the metal. The preferred range of temperature during reduction is from 230° to 270° C., the material being heated for a longer period the lower the temperature employed. It is stated that unnecessarily protracted heating should be avoided as leading to a more complete reduction with loss of activity in the product.

The product may be collected for immediate use in the medium in

* Ellis, U. S. Patent 1,092,206, April 7, 1914.

† U. S. Patent 1,093,377, April 14, 1914.

which it is to be used, e.g., oil, but if not required at once slow oxidation in the atmosphere can be allowed, provided local overheating is prevented (which leads to excessive oxidation) and the material can then be kept without special precautions against oxidation and restored to full activity when required. For instance the material may be collected in water and then filtered therefrom and allowed to dry in the air or may be collected in an atmosphere of hydrogen, which is then slowly replaced by oxygen or air.

In order to prepare it for use the material only requires to be heated for say one to two hours at about 180° C. in an atmosphere of hydrogen or the catalyst may be treated with hydrogen when in suspension in a suitable liquid. When the catalyst is used for hardening fats or oils no special treatment of this kind is necessary as the catalyst acquires its full activity in the early stages of the process.

The catalyst may be prepared by reducing to nickel as completely as possible one of the oxides of nickel and oxidizing this product with air or oxygen diluted with an inert gas, the proportion of oxygen being regulated to avoid local overheating. This oxidizing action can be carried out at between 300° and 600° C.

Boberg states that he has "made experiments with various products of reduction and has obtained the following results: The product of reduction of such a composition that an ultimate analysis gives a proportion of nickel to oxygen corresponding to an imaginary formula $Ni_{9.3}O$, i.e., but little suboxide, produced, in a certain time, hardening of a liquid fat up to a melting point of 40° C., whereas, a product corresponding to an imaginary formula $Ni_{2.65}O$ gave in the same time and for the same material hardening corresponding to a melting point of 58° C. It appeared, however, that with a lesser proportion of nickel in the product, i.e., a composition that apparently indicated the presence of higher oxides, the product was less active, while, at the same time, compounds containing even higher proportions of metallic nickel than that first specified above, viz., $Ni_{9.3}O$, were still less active than the latter."

Boron may be used as a catalyzer according to **Hildesheimer.*** If the material is a gas it is simply mixed with hydrogen and passed over the boron material; if liquid, it is mixed with boron and hydrogen is passed through it. When the addition of hydrogen is completed the boron is separated by filtration and is ready for use again. The catalytic action is assumed to depend upon the intermediate formation of boron hydride BH_3. The rate of conversion is influenced by the temperature and pressure as well as the amount of boron. Cottonseed oil and other unsaturated compounds, such, for example, as ethyl-

* Zeitsch. f. angew. Chem. (1913), Ref. 583.

ene, add hydrogen under these conditions. In place of boron some of its compounds, such as boron hydride, and metallic compounds of boron, such as aluminium boride, may be used. Gases containing hydrogen may be used in place of pure hydrogen.*

On the large scale the manufacture of catalyzers by reduction of the oxide of a metal in a current of hydrogen has been found to bring with it a train of difficulties. A method of reducing catalyzer in a continuous manner † which simplifies the operation to a considerable extent is shown in Fig. 46. A charge of the material to be reduced

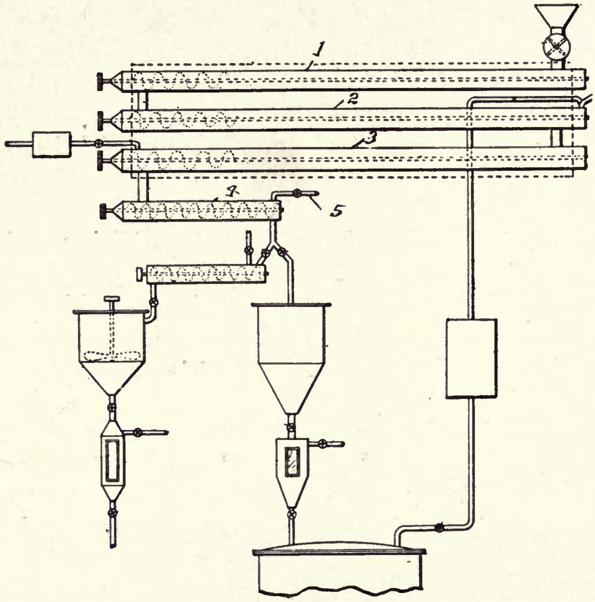


FIG. 46.

is fed from the hopper and feed arrangement into a series of horizontal parallel conveyors 1, 2, 3 and 4 into which a current of hydrogen gas is introduced by the pipe 5. These conveyors connect one with another alternately so that the material travels in one direction through a given conveyor, then falls into the conveyor beneath and travels in

* A process of hydrogenation involving the use of chloride of mercury is described in an Austrian patent application noted in Seifen. Ztg. (1913), 1413. According to the method set forth fatty acids or their glycerides are heated to a temperature below 180° C. with a mixture of a difficultly reducible inorganic salt of a base metal in company with chloride of mercury and at the same time hydrogen or other reducing-gas mixture is passed through the oil.

† Ellis, U. S. Patent 1,078,541, Nov. 11, 1913.

an opposite direction. At the same time the material is heated to the proper temperature of reduction and throughout its travel is in contact with a counter-current of hydrogen. Thus, the more nearly reduced material is constantly progressing into a zone of purer hydrogen, while the fresh raw material meets hydrogen charged with steam. In this manner conditions of reduction are so facilitated that the use

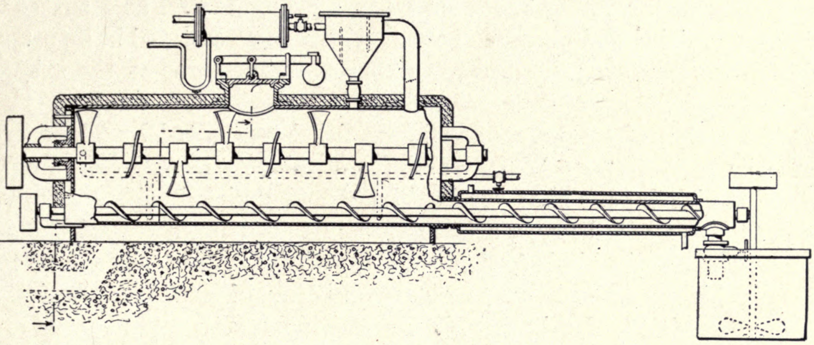


FIG. 47.

of a great excess of hydrogen to remove the steam does not become necessary. After the catalyzer has been reduced it may be mixed with oil in another conveyor and be subsequently carried to a grinder or beating apparatus where the coarser particles are broken down.

Another form of catalyzer reducing chamber is shown in Fig. 47 and consists of a closed chamber equipped with a stirrer and with a conveyor to remove the reduced material.*

* Ellis, U. S. Patent 1,084,202, Jan. 13, 1914.

CHAPTER V

NICKEL CARBONYL

Owing to the interest manifested in nickel carbonyl as a source of catalytic nickel and because of the difficulties encountered in its preparation the following extracts from various publications on the subject are appended.

The action of carbon monoxide on nickel was noted by **Mond** and associates in 1890.* When carbon monoxide is passed over finely-divided nickel, such as is obtained by reducing nickel oxide by hydrogen at about 400 degrees, at a temperature between 350 and 450 degrees, carbon dioxide is formed, and the nickel is gradually converted into a black, amorphous powder, consisting of carbon and nickel; the composition of this deposit varies widely with temperature and time. A small quantity of nickel can thus change a very large amount of carbon monoxide, the action being complete and rapid at first, and continuing, although at a diminishing rate, for several weeks. A product containing as much as 85 parts carbon to 15 parts nickel was obtained. Acids only partially remove the nickel; the carbon is very readily acted on by steam, carbon dioxide and hydrogen without a trace of carbon monoxide being formed at a temperature of 350 degrees.

On allowing the substance to cool in a current of carbon monoxide, it was noticed that the flame of a Bunsen burner into which the escaping gas was introduced became luminous, and when the tube through which the gas passed was heated, a deposit of nickel, mixed with a small quantity of carbon, was obtained. Mond and his associates were thus led to discover the existence of a volatile nickel compound.

To prepare this compound a combustion tube was filled with nickel oxide and this was reduced by hydrogen at about 400 degrees; after cooling the nickel to about 100 degrees, pure dry carbon monoxide was passed over it without further heating, and the issuing gas led through a tube placed in a freezing mixture; the major portion of the nickel compound condensed as a colorless liquid; but since the gas retained about 5 per cent, it was collected, dried and again passed over the metal. When no more liquid condensed, the nickel was again

* Mond, Langer and Quincke, Proc. Chem. Soc. (1890), 112; J. S. C. I. (1890), 808.

heated to about 400 degrees in a slow current of pure carbon monoxide; it was then cooled to about 100 degrees, and again submitted to the action of the gas.

Nickel carbonyl thus prepared is a colorless liquid, which boils at 43 degrees under 751 mm. pressure; its relative density at 17 degrees is 1.3185. It solidifies at -25 degrees to a mass of needle-shaped crystals. Its composition is represented by the formula $Ni(CO)_4$. It dissolves in alcohol, and more readily in benzene and chloroform; dilute acids and alkalis have no action on it, but it is oxidized by concentrated nitric acid. It reduces an ammoniacal solution of cupric chloride, and also causes the separation of silver from an ammoniacal solution of silver chloride. It interacts with chlorine, forming nickel chloride and carbon oxychloride. It is decomposed at 180 degrees (in boiling aniline vapor) into nickel and carbon monoxide. The atomic weight of the deposited metal was found in three experiments to be 58.52 to 58.64, a result closely corresponding with Russell's value, 58.74.

Numerous experiments to obtain similar compounds with other metals, notably with cobalt, iron, copper and platinum, led to negative results. On experimenting with specially-purified cobalt, in the beginning a slight coloration of the Bunsen flame into which the gas was led was noticed, but after a time this was no longer observed. Commercial cobalt afforded a gas which deposited a mirror of pure nickel, it being possible, in fact, to purify cobalt from nickel by carbonic oxide. The nickel mirrors obtained by heating the carbonic oxide compound do not appear to contain any trace of cobalt.

Martha (Chem. Ztg. (1891), 915; J. S. C. I., 1891, 837) has recorded some properties of nickel carbonyl which are of interest. He used some impure ferriferous nickel oxide as the source of the metal. Under these circumstances the condensed nickel compound has always a yellow tinge, and contains iron, as do also the nickel films obtained by heating the conducting tube. The liquid after standing for a few hours, even in a sealed tube, deposits a brown compound containing iron, which often explodes with great violence when the liquid is poured off, the sides of the tube being simultaneously covered with a film of nickel. An apple green precipitate containing nickel is occasionally deposited, together with the brown iron compound, and adheres strongly to the sides of the tube. The vapor of the liquid compound exploded upon one occasion very violently, either owing to the presence of a particle of the iron compound or to its own explosive properties.

Berthelot * notes that the vapor tension of nickel carbonyl (boiling point 46° C.) at 16° C. is about one-fourth of an atmosphere. A drop of the liquid allowed to evaporate spontaneously forms a certain quantity of crystals, which consist of the solidified substance, and speedily volatilize on continued exposure. It has no sensible tension of dissociation at the ordinary temperature, but in contact with air

* Bull. Soc. Chim. (1892), 13, 431.

oxidizes rapidly. The precise mechanism of oxidation varies according to the conditions under which it takes place. For example, when an inert gas, charged with the vapor of nickel carbonyl, is passed through a strongly heated tube, the products are metallic nickel and carbon monoxide, as observed by Mond and his colleagues. These investigators also found when nickel carbonyl is heated sharply to 70° C., at which point detonation takes place, that the same bodies are formed.

Berthelot, however, has observed that a certain amount of carbon dioxide and carbon is produced. He is of the opinion that this reaction determines the occurrence of the detonation, as the equation

$$2\,CO = CO_2 + C$$

implies the evolution of 38.8 calories, i.e., 77.6 calories for the 4 mols. of carbon monoxide in $Ni(CO)_4$. The only assumption necessary to justify this view is that the heat of combination of Ni and CO is less than 77.6 calories.

The reactions of nickel carbonyl are generally those dependent upon the presence in it of nickel, but when they are induced gently and at low temperature, bodies comparable to organo-metallic compounds are formed. The vapor of nickel carbonyl is not sensibly soluble in water or dilute acid or alkaline solutions or cuprous chloride. Hydrocarbons are its natural solvents; spirits of turpentine is specially suitable, and can be used for determining it. Explosion of a mixture of nickel carbonyl and oxygen can be effected by violent agitation over mercury as well as by direct ignition. Slow union takes place when such a mixture is kept in contact with a little water. In contact with strong sulfuric acid dry liquid nickel carbonyl explodes after a short interval, but if in the form of vapor and diluted with nitrogen it is decomposed gradually, the theoretical quantity of carbon monoxide being liberated. Strong caustic potash has no perceptible action on nickel carbonyl. Gaseous ammonia does not act immediately per se, but if a little oxygen be added, fumes are produced, and if the action of oxygen be continued a whitish deposit of complex composition is gradually formed which is destroyed with charring on being heated.

Sulfuretted hydrogen acts on nickel carbonyl vapor, mixed with nitrogen in the cold, a black sulfide (of nickel) being precipitated. Phosphoretted hydrogen under similar conditions gives a brilliant black deposit. Nitric oxide if mixed with nickel carbonyl vapor, diluted with nitrogen, or passed into the liquid itself, produces blue fumes, which fill the whole vessel. The formation of nickel carbonyl proves carbon monoxide to be capable of forming organo-metallic compounds similar to those derived from hydrocarbons, and analogous to the salts of rhodizonic and croconic acids produced by the union of

the condensed derivatives of carbon monoxide with an alkaline metal. Nickel carbonyl serves as an example of the tendency of carbon monoxide to form loose combinations and products of condensation, in virtue of its character as an unsaturated body.

Nickel carbonyl, according to Berthelot,* can be preserved under water, but if contained in a bottle with an ordinary ground-in stopper becomes slowly oxidized, and a layer of apple green nickel hydrate is formed, which is free from carbon. A portion of it, however, makes its way out of the bottle and is oxidized, forming a fume which is deposited on adjacent objects.

In order to examine the product of oxidation Berthelot kept a bottle of nickel carbonyl in a double casing of tin plate and succeeded in collecting a few decigrams of a complex oxide, which appeared white in small quantity, but had a greenish tinge when viewed in mass. It was found to be the hydrated oxide of an organo-metallic compound of nickel, and upon analysis gave figures corresponding to the formula $C_2O_3Ni_3 \cdot 10\ H_2O$. It therefore appears to be the oxide of a complex radical analogous to croconic and rhodizonic acids.

The fact that under ordinary circumstances nickel alone is acted on when a mixture of this metal with any other metallic or mineral substance is treated by carbonic oxide gas, led **Mond** (J. S. C. I., 1891, 836) to institute experiments to ascertain whether it would not be possible by means of carbonic oxide to extract nickel direct from its ores, and such metallurgical products as nickel speiss and nickel matte. As the nickel is volatilized at the ordinary temperature in the form of a vapor disseminated through other gases from which it can be deposited without first condensing the nickel compound, by simply heating these gases to the moderate temperature of 200° C., as it is thus obtained in the form of bright coherent masses of great purity, as the carbonic oxide used is completely liberated and can be employed over and over again, and as small quantities of the poisonous nickel compound which may escape decomposition would thus never leave the closed apparatus in which the process would be carried out, it seemed probable that such a process might be capable of industrial application, and might prove more economical than the complicated operations metallurgists have to resort to to produce tolerably pure nickel.

Experiments carried out in conjunction with Langer, with a great variety of nickel ores from all parts of the world, containing from 4 to 40 per cent of nickel, as well as a number of samples of nickel speiss and nickel matte, proved that as long as the nickel is combined with arsenic or sulfur the process was successful. In the majority of cases Mond was able to extract the nickel almost completely in three or four days. Such ores or matte or speiss have in the first instance to be calcined, so as to convert the nickel completely into oxide. The mass is then reduced in a current of hydrogen-containing gases — in practice water gas at a temperature of 450° C. It is cooled down to ordinary temperature and treated with any good apparatus for treating solids by gases. Methodical apparatus moving the reduced ore in opposite directions to the current of carbon monoxide, at the same time exposing fresh surfaces, facilitate the operation. After a certain time the action of the carbon monoxide upon the nickel becomes sluggish. The mass is then heated to about

* Bull. Soc. Chim. (1892), 434.

350° C. in a current of carbon monoxide, which regenerates the activity of the nickel. This may be done in the same apparatus, but it is preferable to use a separate apparatus connected with the first, and from which the material is returned to the first by mechanical means, so that each apparatus can be kept at the same temperature. The carbon monoxide gas can be employed dilute, as it is obtained from gas producers; but since it is continuously recovered, a purer gas, such as can be cheaply prepared by passing carbon dioxide through incandescent coke, is more advantageous, as it extracts the nickel more quickly and requires smaller apparatus. The gas charged with the nickel compound leaving the apparatus is passed through tubes or chambers heated to about 200° C., in which the nickel is deposited. The gas leaving these tubes is returned to the first apparatus, and circulates continuously. From time to time the nickel is removed from the tubes in which it has been deposited. To facilitate this operation thin nickel sheets, bent to fit the tubes, are inserted, on which the nickel deposits, and which are easily taken out. The metal so obtained is almost chemically pure; only very rarely in the case of certain ores it is slightly contaminated with iron. As the nickel is deposited in perfectly coherent films upon heated surfaces exposed to the gas containing the nickel carbonyl, it was found possible to produce direct from such gas, articles of solid nickel or goods plated with nickel. This result can also be obtained by immersing heated articles in a solution of nickel carbonyl in such solvents as benzole, petroleum, tar oils, etc., or by applying such solution to the heated articles with a brush or otherwise.

Mond * observes that a mixture of the vapor and air explodes readily but not very violently. The pure liquid does not explode, but at high temperatures it decomposes. The vapor has a characteristic odor and is poisonous. It produces an extraordinary reduction of temperature when injected subcutaneously, sometimes as much as 12 degrees. The liquid can be distilled, but not from solution in liquids of a higher boiling point as decomposition then occurs, finely-divided nickel being separated and carbonic oxide being evolved.

When attacked by oxidizing agents, e.g., nitric acid, chlorine, or bromine or by sulfur, decomposition ensues, nickel salts being formed and carbon dioxide liberated. Metals, alkalies, non-oxidizing acids and the salts of other metals produce no change. Nickel carbonates of composition varying with the hygroscopic state of the atmosphere are formed by exposing the liquid to the action of the air. These precipitates dissolve easily in dilute acid. An intense blue coloration is obtained when nitric oxide is passed through a solution of nickel carbonyl in alcohol (Berthelot).

Nickel carbonyl is very diamagnetic, and an almost perfect non-conductor of electricity (Quincke). All other nickel compounds are paramagnetic. It is opaque for rays beyond the wave length 3820, and its flame gives a continuous spectrum (Liveing and Dewar).

Perkin found the power of magnetic rotation of nickel carbonyl to be greater than that of any other substance he has examined, except phosphorus. Mond and Nasini found the atomic refraction to be about 2.5 times as large as in any other nickel compound, and the former proved it to have great refractive and dispersive powers. The atomic refraction of a liquid ferro-carbonyl bears about the same

* J. S. C. I., 1892, 750.

ratio to the atomic refraction of other iron compounds. This ferro-carbonyl is similar in preparation and properties to the nickel carbonyl, and at 180° C. the iron is thrown down in bright mirror-like form, carbon monoxide being liberated. Its composition is $Fe(CO)_5$.

To extract nickel from its ores Mond used an apparatus, Fig. 48, consisting of a cylinder divided into many compartments, through which the properly prepared ore is passed very slowly by means of stirrers attached to a shaft. On leaving the bottom of this cylinder the ore passes through a transporting screw, and from this to an elevator which returns it to the top of the cylinder, so that it passes many times through the cylinder until all the nickel is volatilized. Into the bottom of this cylinder carbonic oxide is passed, which being charged with nickel carbonyl vapor leaves at the top, and passes through the conduits shown into tubes set in a furnace, and heated to 200° C. Here the nickel separates from the nickel carbonyl. The carbonic oxide is regenerated and taken back to the cylinder by means of a fan, so that the same gas is made to carry fresh quantities of nickel out of the ore in the cylinder, and to deposit it in the tubes an infinite number of times. When the carbonic oxide comes out at the top of

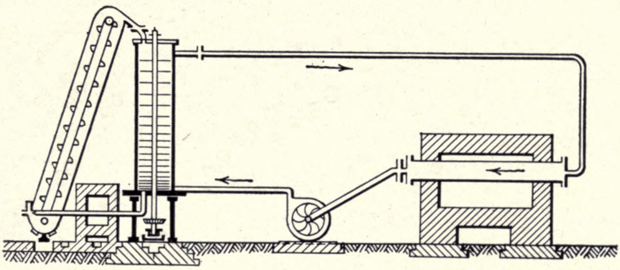


Fig. 48.

the cylinder it passes through a filter to catch any dust it may contain. The carbonic oxide, on escaping from the depositing tubes, is passed through another filter, thence through a lime purifier to absorb any carbon dioxide which may have been formed. By means of this apparatus nickel has been extracted from a great number of ores, in times varying, according to the nature of the ores, from a few hours to several days.

A review by Mond of his experimental work on nickel carbonyl * is instructive.

* J. S. C. I., 1895, 945.

Mond stated that "in the course of these experiments finely-divided nickel, formed by reducing nickel oxide at 400° C. by hydrogen, was treated with pure CO in a glass tube, at varying temperatures, for a number of days, and was then cooled down in a current of CO before it was removed from the tube. In order to keep the poisonous CO out of the atmosphere of the laboratory, we simply lit the gas escaping from the apparatus. To our surprise we found that, while the apparatus was cooling down, the flame of the escaping gas became luminous and increased in luminosity as the temperature got below 100° C. On a cold plate of porcelain put into this luminous flame, metallic spots were deposited similar to the spots of arsenic obtained with a Marsh apparatus; and on heating the tube through which the gas was escaping we obtained a metallic mirror, while the luminosity disappeared."

"At the first moment we thought that there must be an unknown element in our nickel giving rise to the production of this effect, but when we examined the mirrors we found them to consist of pure nickel. As it seemed so very improbable that so heavy a metal as nickel should form a readily volatile compound with CO, we purified our CO as perfectly as possible but still obtained the same results."

"We now endeavored to isolate this curious and interesting substance by preparing the nickel with great care at the lowest possible temperature, and treating this nickel with CO at about 50° C., and thus we gradually increased the amount of the volatile nickel compound in the gases passing through the apparatus. We absorbed the excess of CO by cuprous chloride solution, and thus obtained a residue of several cubic centimeters, containing the volatile nickel compound mixed with a little nitrogen. By passing this gas through a heated tube we separated the nickel, obtaining an increased volume of gas, and found in this a quantity of CO corresponding to about four equivalents for one equivalent of nickel. By further improving our method of preparing the finely-divided nickel and by passing the resulting gas through a refrigerator, cooled by snow and salt, we at last succeeded in liquefying this compound, and were able to produce it with ease and facility in any quantity we desired." Nickel carbonyl "is soluble in alcohol, petroleum and chloroform; it is not acted upon by dilute acids or alkalies, and can be readily distilled without decomposition. But on heating the gas to 150° C., it is completely dissociated into its components, pure CO being obtained and the nickel being deposited in a dense metallic film upon the sides of the vessel in which it is heated."

"For a long time, while we were engaged in investigating the physical and chemical properties of this interesting substance — which was without parallel in the history of chemistry — and while we were endeavoring to obtain other similar compounds with other metals, I had myself no suspicion that this substance, which was until then only obtainable by very careful and elaborate laboratory manipulations, should ever become available for industrial purposes. But the longer we went on preparing it for our investigations, the more easy we found it to prepare it in quantity, after we once knew exactly the best conditions for so doing. After that I came to the conclusion that it ought to be possible to make use of the ease with which nickel is converted into a volatile gas by CO, while practically all other metals, and notably cobalt (which is so difficult to separate from nickel by other methods), was not acted upon by this gas, for separating nickel from cobalt and other metals on a manufacturing scale, and for obtaining it in a very pure state."

"I erected a plant on a large scale near Birmingham, and after several years of hard work, during which the apparatus has had to be several times reconstructed so as to fulfil all the conditions of this rather delicate process, we have succeeded in our object, and now have for some time produced nickel at the rate of a ton and

a half per week from the Canadian nickel copper matte imported into England. This matte, which contains about 40 per cent of nickel, and an equal quantity of copper, is carefully roasted to drive out the sulfur as far as possible, and is then subjected to the action of hydrogenous gases, either water gas or producer gas, rich in hydrogen, in an apparatus which is called the 'reducer,' the temperature of which is under perfect control, so that 400° C. is never exceeded. From this apparatus the substance, which is now reduced to the metallic state, is taken through air-tight conveyors and elevators into another apparatus called the 'volatilizer,' in which it is subjected, at a temperature not exceeding 80° C., to the action of CO gas."

"This apparatus consists of an iron cylinder, divided into numerous compartments by shelves, and provided with a stirring device, which gradually moves the material from the top to the bottom, while the CO gas passes through in an opposite direction. The CO gas, which should be as rich as practicable, we prepare by passing pure CO_2 through incandescent coke; the pure CO_2 we make by passing the flue gas of a boiler or of a fire through a solution of carbonate of potash, and subsequently boiling the solution. The CO gas, charged with nickel carbonyl, leaving the volatilizer, is passed through a series of tubes or chambers, heated to about 180° C., in which the nickel is deposited in various forms, according to the speed of the gas current, the richness of the gas and the existing temperature. The CO gas, thus almost completely freed from the nickel, is taken back by means of a blower into the volatilizer, where it takes up a fresh quantity of nickel and is constantly used over and over, so that the quantity consumed is limited to the very small amount of unavoidable loss through leakage of the plant."

"The material under treatment is repeatedly taken from the volatilizer to the reducer and vice versa, by means of air-tight conveyors and elevators, until the amount of nickel volatilized begins to fall off. It is then roasted again to remove the sulfur which it still contains, and is treated by sulfuric acid to dissolve part of the copper. The residue, containing nickel, some copper and the other impurities of the matter is again subjected to the previously described treatment until the nickel has been extracted as far as practicable; and the ultimate residue, still containing a few per cent of nickel, is melted up into matte again."

Nickel carbonyl is decomposed * by passage through a mass of pellets of metallic nickel, heated to about 200° C., causing nickel to be deposited and the pellets to increase in size. The apparatus consists of a vertical cylinder, in which the pellets are placed, with heating spaces formed by an outer casing. A vertical, cooled, perforated tube for the gaseous carbonyl leads from the top down the center of the mass of pellets, nearly to the bottom of the cylinder. To prevent the pellets cohering, they are kept in motion by continuously withdrawing them from the lower end, mechanically screening them with the assistance of worm conveyors, and returning the small ones by an elevator to a feeding hole at the upper end for further treatment with the carbonyl. The pellets which have sufficiently increased in size are passed from the screen and thence through a valved opening into a collecting chamber.

* Mond, British Patent 1106, Jan. 14, 1898.

In extracting nickel by means of carbon monoxide from mixtures of nickel and other metals, obtained by reducing the mixed oxide with gas containing carbon monoxide, **Fierz** * displaces the carbon monoxide by hydrogen or removes it by suction from the presence of the reduced metals while the temperature is maintained above that at which nickel will decompose, or combine with, carbon monoxide. The temperature is then reduced to that required for the formation of nickel carbonyl and the gas readmitted.

Langer † describes an apparatus for obtaining nickel from nickel carbonyl. Vessels containing the nickel carbonyl are heated by a number of gas flames, each of which is situated in a chamber formed by ribs on the vessel and an outer casing; the liberated gases pass away by an escape pipe, which is surrounded by an annular cooling chamber.‡

James Dewar § remarks that the nickel carbonyl vapor at ordinary pressures is very unstable, its components becoming rapidly dissociated with explosion on moderate elevation of temperature, so that its production has hitherto been carried on at a moderately low temperature, such as 50° C. Dewar has found that under considerable pressure, ranging from 2 atmospheres to 100 atmospheres, the compound, either as vapor or as liquid, is much more stable, and therefore higher temperatures can be used in its production, whereby the rapidity of process of manufacture is greatly increased. Thus for the gasification of the nickel a temperature of 100° C. with a pressure of 15 atmospheres is suitable, or a temperature of 180° C. with a pressure of 80 atmospheres. The spongy nickel obtained by the reduction by means of water gas, if treated at the temperature and pressure mentioned, combines rapidly with the carbonic oxide, producing vapor of nickel carbonyl. This vapor, with the excess of carbonic oxide in which it is diffused while still under pressure, on being passed through tubes of a higher temperature, becomes dissociated depositing metallic nickel.‖

In the author's laboratory nickel carbonyl has been extensively examined and has proved a satisfactory source of nickel catalyzer. The carbonyl readily decomposes at temperatures between 125° and 180° C. and when decomposed in the presence of oil under some conditions the resulting nickel is very finely divided and imparts to the

* British Patent 4249, Feb. 19, 1913.

† British Patent 13,350, June 28, 1905.

‡ See also U. S. Patent 815,717, Mar. 20, 1906; 825,844, July 10, 1906; and 865,969, Sept. 10, 1907.

§ U. S. Patent 760,852, May 24, 1904.

‖ Electrochem. and Met. Ind. (1904), 291.

oil an inky black color. Even after standing for days or even weeks the nickel remains in suspension. A sample of cottonseed oil carrying about one-half of one per cent of nickel precipitated from nickel carbonyl was exposed to the action of a current of hydrogen gas under practically atmospheric pressure for a period of one hour and a solid product resulted having a melting point of 47.6° C. and a refractive index of 1.4445.

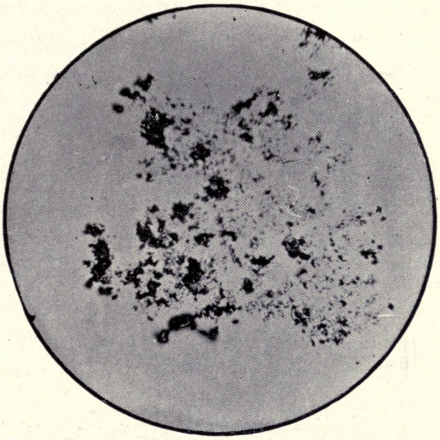


FIG. 49. — Photo-micrograph of Nickel Catalyzer derived from Nickel Carbonyl. × 100.

The greatest difficulty in the use of nickel carbonyl appears to be the removal of finer portions of the nickel precipitate from the oil after hydrogenation, but this may be accomplished by the observance of due precaution in filtration. The used catalyzer recovered by filtration is still active and may be used until its catalytic properties are spent. The spent material may be regenerated more easily than is the case with catalyzers consisting of nickel supported on a voluminous carrier of inert material.*

* Apparatus adapted for handling nickel carbonyl and hydrogenating oils with the nickel material obtained by its decomposition is shown in U. S. Patent to Ellis, 1,095,144, Apr. 28, 1914.

CHAPTER VI

THE RARE METALS AS CATALYZERS

As a catalyzer in this field palladium has received considerable study, for, in spite of high first cost, its pronounced effectiveness, together with its ability to effect hydrogenation at relatively low temperatures, makes it particularly attractive.

Many years ago, **Fokin** * stated that he regarded palladium as the most powerful of all catalyzers, having found that reduction takes place readily at 80° to 90° C., while with nickel, a temperature of 180° to 200° C. was necessary for practical hydrogenation. Fokin's experiments at that time were concerned with electrolytic reduction. By this means he reduced linseed, wood, castor and cod liver oil. He found that while *palladium* black would reduce oleic acid completely to stearic acid, *platinum* black under the same conditions gave only 24 per cent of stearic acid.

Paal † worked with colloidal palladium preparations and hydrogenated castor, olive, fish oil and animal fats. He found that sesame oil, after hydrogenation, showed the Baudoin reaction only very faintly, while cottonseed oil no longer responded to the Becchi and Halphen reaction. Skita has worked with palladium incorporated with a protective colloid.

Paal recommends ‡ platinum or palladium chloride admixed with a neutralizing agent such as sodium carbonate. He states that the reduction of fats and unsaturated fatty acids of animal and vegetable origin may be effected by allowing hydrogen to act on these, in presence of platinum metals, or protohydroxide compounds of the latter, which have been deposited upon certain finely-divided substances and act as catalyzers or carriers of hydrogen. It has also been ascertained that the reduction of the fats and fatty acids may be effected by hydrogen in presence of solid salts of the platinum metals. Both the simple salts, such as palladium protochloride ($PdCl_2$), platinum protochloride ($PtCl_2$), platinum chloride ($PtCl_4$), platinum hydrochloride (H_2PtCl_6), platinum sulfate and the double salts, for instance potassium

* Chem. Ztg. [2], 1906, 758; [1], 1907, 324.
† Ber., 41, 2282.
‡ U. S. Patent 1,023,753, April 16, 1912.

chloroplatinate (K_2PtCl_6), copper platinochloride, may be used. When the double salts are used, care must be taken that no anticatalytic substances, such for instance as lead, find their way into the reduction mixture. Use may be made of salts whose acid radicals or other constituents are themselves reduced by hydrogen, for example acid platinous oxalate. In all cases the method is simple; and it is distinguished from those in which the finely-divided metals are used by the omission of the preparation of the finely-divided platinum metals or their protohydroxides and of the deposition on special carriers.

The salts in a crushed condition, preferably in the state of powder, are mixed with the fats or fatty acids to be hydrogenated; and hydrogen is allowed to act on this mixture, with stirring, at temperatures below 100 degrees preferably under a pressure of several atmospheres. In a short time the solid reduction product of the fat or fatty acid will be obtained. All that is necessary to insure the action of the solid salts of the platinum metals is that they must be present in the solid form during the progress of the reaction. The salts may also be added to the fats in a dissolved condition (for example in aqueous solution), the solvent being evaporated before or at the beginning of the reduction process. A suspension of the solid salts may also be used. For example, the salts of the platinum metals may be triturated with a portion of the fat or oil that is to be reduced, the mixture being then added to the main portion of the fats or fatty acids to be reduced. Or a suspension of the salts in mineral oil may be prepared, and this mixture may be added to the substances that are to be reduced, in which case the suspensory medium may be eliminated during the process of reduction. A single salt of a platinum metal may be used, or several salts, and even several platinum metals may be mixed together; and the salts may also be used in conjunction with the platinum metals which have been deposited on carriers, devoid of anticatalytic action, such as copper, or magnesium carbonate. It is probable that, during the process, the salts of the platinum metals are split up into metal and free acid, for example:

$$PdCl_2 + H_2 = Pd + 2\,HCl.$$

In any case, however, the solid platinum metal salts greatly facilitate the absorption of hydrogen by fats and fatty acids. Very small quantities of the platinum-metal salts are sufficient to reduce large quantities of fat or fatty acids in presence of hydrogen. When the reduction process is completed, the platinum metals or their compounds can be easily separated from the reduced fat or fatty acid by filtration, and used again.

To prevent the formation of free acid, as, for example, hydrochloric acid from the chlorides of the platinum metals, in the reducing process, there is added to the powdered platinum salt a neutralizing agent, such as anhydrous soda, in sufficient quantity to combine with the liberated acid. The employment of salts of the platinum metals assists the reduction process considerably more than is done by palladium black or platinum black containing an amount of platinum metal equal to that in the platinum metal salts used in the present method. Thus, for example, 1.7 parts of $PdCl_2$ (= 1 part of Pd) in presence of hydrogen will convert 10,000 parts of fat or fatty acid into solid masses within 3 or 4 hours. If, however, the $PdCl_2$ be

replaced by a quantity of palladium black containing the same amount of palladium, then, with a ratio of 1 part of Pd to 10,000 parts of fat or fatty acid, these substances, according to Paal, will remain liquid, even when the palladium and hydrogen are allowed to act for twice or three times as long as with $PdCl_2$.

Paal notes that the time required for the reduction depends on the amount of the platinum metal salt used, and on the pressure under which the hydrogen is allowed to act. By using a palladium salt as the hydrogen carrier, about 50,000 parts of fat or unsaturated fatty acid can be hydrogenated within from 6 to 8 hours with a quantity of salt, for example, $PdCl_2$, corresponding with 1 part of Pd.

Paal gives the following example: One million parts by weight of castor oil or oleic acid are treated with thirty-four parts by weight of dry palladium protochloride (= 20 parts of Pd) in the form of powder, with or without the equivalent amount of anhydrous soda; or with 140 parts by weight of dry platinum protochloride (= 100 parts of Pt) in the form of powder; or 172 parts of platinum chloride; or 230 parts of platinum hydrochloride, with or without addition of an equivalent amount of anhydrous soda. The mixture is placed in a pressure vessel, from which the air is exhausted as completely as possible, and hydrogen is then admitted into the vessel under a pressure of 2 to 3 atmospheres. The reduction mixture is kept in motion by a stirring apparatus. The vessel is heated to about 80° C. although the reduction may also be carried out at a lower temperature. The progress of the reduction and the consumption of hydrogen is revealed by the fall in pressure as indicated by the pressure gauge. When the gauge registers only a low pressure, a fresh quantity of hydrogen is admitted. The completion of the reduction process can be recognized by the gas pressure remaining constant for some considerable time. When the reduction is ended, the reduction product is freed from the catalyzer in a filter press which is adapted to be heated.

The work in the field of catalytic reduction of organic compounds has been rather comprehensively covered in a publication by **Skita** entitled "Uber Katalytische Reduktionen Organischer Verbindungen (Stuttgart, 1912). Skita has taken out a patent assigned to Boehringer and Son * which is concerned with the hydrogenation of organic compounds with the aid of catalyzers consisting of salts of the platinum group of metals. The protective colloid previously employed he now finds to be unnecessary. He states he has found that an unsaturated substance can be hydrogenated when there is added to it, or its solution or suspension, a small amount of palladium chloride or any other soluble salt of a platinum metal and the whole exposed to hydrogen, most advantageously under pressure. The addition of an acid is usually advantageous in this operation and hydrochloric acid is recommended; but with fatty bodies it suffices merely to add a simple aqueous solution of a compound of a metal of the platinum group. As an example, he states, that 50 grams of olive oil may be suspended in a solution containing about 0.05 gram of platinum chloride, 20 cc. of alcohol, 50 cc. of water and 8 cc. of dilute hydro-

* U. S. Patent 1,063,746, June 3, 1913.

chloric acid. After treatment with hydrogen at a pressure of about 4 atmospheres and at a temperature of 70° C. a solid fat results. In another example about 250 grams of castor oil is well mixed with a solution of about 0.05 gram of palladium chloride in 5 cc. of water. The whole may then be treated at about 70° C. in an autoclave with constant stirring, with hydrogen under a pressure of 4 atmospheres. After two and one-half hours the oil will be found so far hydrogenated that it will solidify to a hard mass on cooling.*

In an address before the Chemical Society of Karlsruhe Dr. Skita made the following comments on the hydrogenation of organic material.†

He stated that the acceleration which various reactions experience in the presence of catalyzer is the more rapid the greater the surface of the catalyzer. As a result a catalyzer in solution is always more active than is the case when the catalyzer is in a finely-divided or precipitated state. This especially is true with metals of the platinum group which exert an action of a very marked character when in solution in the colloidal condition.

Colloidal platinum was first produced by Bredig by the action of an electric current on metallic platinum in aqueous or ethereal solution. Bredig recognized the property which these colloidal solutions possessed of serving as a carrier for hydrogen and he in fact reduced nitrous acid to ammonia. Such colloids are not reversible, that is to say if the colloidal solution is evaporated to dryness the metal will not again go into solution. A metal colloid which is easily soluble in water was discovered by Paal who made use of a water-soluble protective colloid, namely, the sodium salts of protalbinic or lysalbinic

* The hydrogenation of unsaturated substances is effected, according to Skita, by treatment with hydrogen in the presence of small quantities of compounds of metals of the platinum group in solution. The substances to be hydrogenated may be dissolved or suspended in a liquid (French Patent 447,420, Aug. 20, 1912; also British Patent 28,754, Aug., 1912, and addition to the latter Patent 18,996 (1912). A solution of palladium chloride acidulated with dilute hydrochloric acid was used by Skita as a catalytic solution for the treatment of camphene. Hydrogen was used under a pressure of one atmosphere. The hydrogenation of olive and castor oil in this manner is described. In the addition patent Skita states that the employment of dilute acid is not always necessary since in many cases the reaction can be carried out simply by passing hydrogen through a mixture of the substances to be reduced and a solution of the salt. J. S. C. I., March 15, 1913, 253.

Skita (Chem. Zeit. Rep. (1913), 680; British Patents 18,996, 1912, and 16,283, 1913) carries on reduction processes without the addition of any acid to a solution of a salt of the platinum group and also makes use of colloidal solutions of an hydroxide of the platinum group as a catalyzer.

† Seifen. Ztg. (1913), 960.

acids, to maintain the metallic platinum or palladium in a water-soluble condition.*

With colloids of this character prepared from palladium Paal succeeded in adding hydrogen to a large number of unsaturated aliphatic compounds which were soluble in water or dilute alcohol. For the reduction of many organic compounds, such as acids, bases and hydrocarbons, the presence of acid material is of importance and accordingly Skita has used an acid-stable protective colloid such as gum arabic in place of the sodium salts mentioned above. If gum arabic is added to a solution of platinum chloride, no platinum hydroxide is precipitated when carbonate of soda is added to the solution, for the platinum remains suspended in the colloidal condition.

By careful evaporation platinum compounds may be obtained as black plates or scales which are soluble in water and dilute acids. When these colloidal solutions of the hydroxide are agitated in the presence of hydrogen a very acid-resistant form of colloidal platinum results. On evaporation a form of platinum is obtained which is easily soluble in water. All such platinum and palladium compounds are eminently adapted to catalytically transfer hydrogen to unsaturated material contained in an acid or neutral vehicle. It is especially easy to add hydrogen to the double bonds of aliphatic and hydrocyclic hydrocarbon compounds. This is the case as regards the reduction of alkaloids.

Another interesting observation is that very stable colloidal solutions of platinum may be obtained readily by passing hydrogen through such colloidal solutions of platinum containing gum arabic, even when the solution is cold. In a similar manner colloidal solutions of palladium are produced from palladium chloride.

Finally it may be mentioned that in this way hydrogen may be added to aromatic and heterocyclic compounds which cannot be hydrogenated with platinum black catalyzer.†

* Colloidal solutions of gold, silver, platinum, palladium, copper, lead, iron, zinc, tin, nickel, aluminum, magnesium, bismuth, antimony and cadmium, respectively, have been prepared with great ease by an electrical disintegration method, using a high-frequency alternating arc, the leads to which were taken from two points on the inductance of the oscillatory circuit of a Poulsen arc as used in wireless telegraphy. By varying the conditions it was possible to obtain currents of from 0.14 to 15 amperes and E.M.F. of 480 to 4080 volts, and colloidal solutions showing a wide range of colors were thus obtained from a number of the metals. (Morris-Airey and Long, Proc. Univ. Durham Phil. Soc. (1912–1913), **5**, 68; J. S. C. I. (1913), 1015.)

† In his dissertation entitled "Über katalytische Hydrierungen organischer Verbindungen mit kolloidem Palladium und Platin," Meyer draws the following con-

Colloidal suspensions of the metals * have proved excellent catalyzers, effecting many of the reactions which are brought about by enzymes. The analogy between the action of the finely-divided metals and the organic enzymes is strikingly illustrated by the behavior of poisons on the two. The same substances which poison the ferments and which retard the rate at which they decompose hydrogen dioxide, also poison platinum and retard the rate at which it effects the same decomposition. Thus mercuric chloride and hydrocyanic acid in the merest traces poison the organic enzymes. The same quantities produce almost exactly the same effect on the finely-divided metals, with respect to their power to decompose hydrogen dioxide.†

clusions. Methods of reduction depending on the use of a solution of palladious chloride and gum arabic in water-alcohol mixture, forming colloidal palladium with hydrogen, do not progress satisfactorily unless bodies are present which are capable of forming addition compounds with palladious chloride. The action of hydrogen on a hot solution of palladium chloride and a protective colloid gives rise to a colloidal solution of palladium. From colloidal palladium or platinum solutions using gum arabic or gelatine as a protective colloid, the corresponding reversible metal colloid is obtained. With the aid of gum arabic or gelatine as a protective colloid it is possible to obtain permanent colloidal solutions of palladium and platinum hydroxide. By careful evaporation and drying of these colloidal solutions solid products are obtained which may be brought again into colloidal solution by peptization. Stable colloid solutions of palladium may be advantageously obtained by the reduction of dialyzed colloid palladious hydroxide solutions. For the production of a colloidal solution of platinum it is recommended that reduction of chlorplatinic acid by hydrogen in the presence of a protective colloid be employed, in which case the mixture should first be inoculated with small amounts of colloidal platinum or palladium. Colloidal solutions of platinum and palladium with gum arabic or gelatine as a protective colloid are well adapted to the hydrogenation of olefine bodies. The hydrogenation of aromatic bodies with colloidal metallic platinum is possible only in strong acetic acid solutions. The hydrogenation of aromatic bodies is carried out more easily with platinum than with palladium. While gum arabic is suitable for use as a protective colloid with platinum or palladium in the hydrogenation of certain organic bodies, it is found that gelatine under some conditions acts as a catalyzer poison. Vulcanized rubber also affects the activity of the catalyzer. The inoculation method for the production of colloidal solutions of platinum affords a convenient laboratory procedure for the hydrogenation of aromatic bodies as the formation of the colloidal solution and the process of hydrogenation follow one another quickly. The hydrogenation of aromatic bodies using colloidal platinum as a catalyzer progresses three or four times quicker than when platinum black is employed. See also J. S. C. I. (1913), 46, and Ber. (1912), **45**, 3379.

A solution of colloidal platinum is capable of causing the union of hydrogen and oxygen. (Ernst, Zeitsch. physikal. Chem. (1901), **37**, 448.) Ethylene unites with hydrogen even in the cold, in the presence of platinum sponge. (De Wilde, Ber. 7, 354.)

* Jones, A New Era in Chemistry.

† Measurements have shown that the decomposition of hydrogen dioxide by metals

Karl * has studied with considerable care and in a quantitative way the action of palladium supported on various bodies. He found that palladium precipitated on finely-divided nickel or magnesium proved effective catalytically, while if precipitated on lead, aluminum, iron, or zinc, little or no hydrogenation was effected, owing to the anti-catalytic action of these metals. While metallic zinc is anticatalytic, zinc oxide and carbonate have no such effect. In these investigations Karl worked principally with fish, cotton and castor oil and oleic acid.†

is a reaction of the first order, that is, the metal, strictly speaking, does not enter into the reaction at all, only the mass of hydrogen dioxide present undergoing change.

A hydrogenizing ferment in the animal organism capable of transforming nitrobenzene into aniline has been observed by Abelous and Gerard (Comptes Rend., **130** (7), 420). A clear aqueous extract of horse's liver, in presence of chloroform and in an atmosphere of hydrogen, reduced nitrobenzene to aniline, while the same extract, previously boiled, was without action. Abelous and Gerard have previously shown (J. S. C. I., 1899, 871) the deoxidizing action of this ferment, but have had no instance of hydrogenation under its influence. (See also Chandler, J. S. C. I., 1913, 73.)

* Inaugural Dissertation, Erlangen, 1911.

† Paal and Karl (Ber. (1913), 3069; Chem. Ztg. Rep. (1913), 642) tested palladium on various carriers as catalytic material for hardening fats and have found that the oxides, hydroxides and carbonates of lead, cadmium, zinc, aluminum and iron have an anti-catalytic action similar to the metals which they contain. The corresponding compounds of nickel and cobalt, and also magnesium oxide, were investigated. These carriers were coated with palladium by mixing with a solution of palladium chloride in a weak aqueous solution of hydrochloric acid at room temperature, or slightly warmed. Palladious hydroxide was thus precipitated and reduction was obtained by treatment of the powder, which was first moistened with ether, to the action of hydrogen at room temperature. The catalyzer was mixed with fatty material without permitting contact with the air and reduction was carried out in an agitator in an atmosphere of hydrogen. Magnesium oxide did not retard the catalytic action of palladium. In fact, the reduction process appeared to be somewhat increased by the presence of this material.

Paal and Windisch carried on similar experiments with platinum. (Ber. (1913), 4010.) Metal powders of various sorts were purified with alcohol and ether and then platinized by shaking with a solution of chlorplatinic acid. Metallic oxides and carbonates were platinized by the action of sodium carbonate and hydrazine hydrate on a solution of chlorplatinic acid containing the oxide or carbonate in suspension. These products as catalyzers in the hydrogenation of cottonseed oil were found to have differing degrees of catalytic action, and only nickel and magnesium had no influence on the activity of the platinum. The platinum was much less active in the presence of aluminum, cobalt and bismuth, and was rendered completely inactive by iron, copper, zinc, silver, tin and lead. Of the oxides and carbonates examined, only the magnesium compounds were without influence.

Wieland (Ber. (1912), **45**, 2615) considers palladium black less sensitive to "poisons" than platinum black, for in presence of the former a sample of benzene containing thiophen absorbed hydrogen at a noticeable rate although not so rapidly as pure benzene.

A long list of salts available as catalyzers is given in German Patent 260,885 * embracing the sulfates, nitrates and chlorides of platinum and palladium, and double salts of these with alkali chlorides and other chlorides, also certain complex compounds of these metals. The salts are added in an undissolved state directly to the oil to be hardened and subsequently a neutralizing agent also undissolved is added. The temperature is maintained below 100° C. When employing double salts care should be taken to have no anticatalytic substances, such as lead, present in the mixture. Salts, such as acid oxalate of platinum, whose acid radical is capable of reduction, may be used.† If necessary, a solid neutralizing agent may be added (cf. Paal).

The Seifenseider Zeitung, 1912, 550, makes mention of a German Patent application for a process of making hardened fats, using as catalyzers platinum and platinum hydroxide in the form of precipitates and on inert carriers in place of the corresponding compounds of palladium.

In order to avoid the accidental introduction of air or mercury when reducing by means of hydrogen and colloidal platinum a special apparatus has been constructed by Stark (Ber. 1913 (46), 2335). It consists of a glass vessel with two necks, each provided with a glass stopcock. A small funnel with a stopcock is fused into the upper part of the vessel between the two necks. One neck is connected with the source of hydrogen, the other with a graduated gas burette and mercury reservoir. The substance to be reduced is placed in the glass vessel and a current of hydrogen passed through. At this stage the burette and reservoir contain no mercury. The hydrogen supply is then cut off and mercury is poured into the reservoir from which it flows and partly fills the burette. By lowering the reservoir a solution of platinum or palladium can be introduced through the funnel with the stopcock without admitting any air.

Lehmann carries out the hydrogenation of oils or unsaturated fatty acids by passing hydrogen through oil containing a small amount of osmium tetroxide, while the oil is being heated. Osmium dioxide forms from the tetroxide, producing a colloidal solution which can be removed by animal charcoal. In one experiment 10 grams olive oil

Cf. Windisch, Ueber die Hydrogenisation ungesättigter organischer Verbindungen durch Platin und Palladium-wasserstoff und die antikatalytische Wirkung von Fremdstoffen auf den Hydrogenisierungsprozess. Erlangen, 1913.

Dissertation: Schwarz, Erlangen, 1913, publishes work on colloidal platinum and the effect of anti-catalytic bodies. J. v. Bergen, Karlsruhe, 1913, gives results of work with palladium hydrosols.

* Seifen. Ztg., 1913, 851.

† Fokin has used the compound $PdCl_2.2\ NaCl$ as a catalyzer (Russian Patent 22,629, Sept. 30, 1912; Chem. Ztg. Rep., 1914, 40).

with 0.05 gram osmium tetroxide produced in $1\frac{1}{2}$ hours a fat of melting point 39° C. It is not necessary to use hydrogen under pressure.*

Besides palladium and platinum the metals iridium, rhodium, ruthenium and osmium are specified as catalytic material.† Madinaveitia‡ has studied the catalytic activity of ruthenium, rhodium, iridium and osmium black.

In connection with the volumetric determination of hydrogen by catalytic absorption in a solution of sodium picrate and colloidal palladium Paal and Hartmann § note that oxygen and unsaturated hydrocarbons must be removed, for in presence of palladium, hydrogen reacts with them to form water and paraffin hydrocarbons respectively; and carbon monoxide should also be removed, as it acts as a " poison " on the catalyst, and greatly retards the absorption.

Colloidal solutions of hydroxides of metals of the platinum group, obtained by treating a solution of a salt of the metal with sodium carbonate in presence of gum arabic, are found by Skita (British Patent 16,283, July 15, 1913) to be efficient hydrogen carriers in the hydrogenation of unsaturated compounds, the reaction being possible even in neutral solutions. In this manner it is stated that unsaturated fatty acids or fats can be hydrogenated to any degree. For example, a hard fat is obtained by passing hydrogen at a pressure of seven atmospheres into a mixture of 50 parts (by weight) of peanut oil and 60 parts of a colloidal solution of palladious hydroxide, containing about 0.07 part of the hydroxide, at a temperature of 60° C.

* Arch. Pharm. (1913), 152; Seifen. Ztg. (1913), 418.

† Vereinigte Chemische Werke A. G. French Patent 425,729 (1911); Seifen. Ztg. (1912), 390.

In using platinum or palladium the following example is given: 1000 kilos castor oil are mixed with 1 kilo of catalyzer which contains 1 per cent of palladium or 2 per cent platinum either in the metallic state or in the form of the lower hydroxide. This mixture of oil and catalyzer is placed in a closed receptacle equipped with an agitator. Any moisture present is removed as completely as possible and then hydrogen is introduced, creating a gas pressure of 2 to 3 atmospheres. The contents of the receptacle are heated to 80° C. and the agitator put into operation. Hydrogen is introduced as required. The hydrogenation of fatty acids may be carried out in a similar manner, but care should be taken to use catalytic material containing palladium or platinum which is not attacked by acids. One composition mentioned for the purpose is prepared by mixing barium chloride with palladium or platinum chloride to which is added sodium sulfate and some hydroxylamine or other reducing agent. For the production of oleic acid one part of catalyzer carrying 1 per cent of palladium or 2 per cent platinum is used to 1000 parts of the fatty acid.

Palladium in various metallic forms as a catalyzer is mentioned in Seifen. Ztg. (1914), 7, as forming a basis of a patent application by the Naamlooze Vennootschap Ant. Jurgens Vereenigde Fabrieken. See German Patent 272,340, 1912.

‡ Chem. Abs., 1914, 1106.

§ Ber. (1910), 43, 243.

Thron * adds hydrogen to unsaturated bodies with the aid of a finely-divided metal of the platinum group and formic acid. The latter is split by the platinum metals by catalytic action into carbonic acid and hydrogen, the latter, it is stated, causing the formation of a compound of the platinum metal and hydrogen (hydride of the platinum metal). By adding to the substance to be hydrogenized formic acid and, for example, palladium black, the development of carbonic acid begins at once, while hydrogen is combined with the unsaturated bodies present.

A platinum catalyzer used by **Porter** (U. S. Patent 684,863, Oct. 22, 1901) for igniting combustible gas is prepared by mixing platinum black with the oxide of zirconium in about the proportion of twenty-five per cent of platinum to seventy-five per cent of zirconium oxide. To prepare this, the platinum in a state of solution is mixed with the oxide of zirconium and the liquid is evaporated, leaving the platinum compound distributed throughout the mass. This is then applied to some incombustible substance, such as asbestos or mineral wool, which forms a convenient support for the substance. After heating, the platinum remains in a finely-divided state. **de Montlaur** used mica as a support for platinum, Zeitsch. f. angew. Chem. (1914), 61, No. 7.

A catalyzer capable of bringing about reaction between air and ammonia to form nitric oxide has been proposed by **Schick** (U. S. Patent 971,149, Sept. 27, 1910) and is based on the use of platinum coated on a suitable carrier such as quartzite, porcelain and the like. The spongy form of platinum is not useful for the purpose, owing to undesirable side reactions taking place in the center of the spongy mass. Accordingly a very thin surface layer of platinum is deposited on the carrier, and to get a coating of sufficient thickness the carrier is coated with a glaze such as a mixture of felspar and an alkali that will soften easily when heated. The platinum material is then baked on the carrier in the presence of this glaze which brings about the formation of a uniformly thin layer of the metal. A temperature of 1400° C. is used.

In discussing the properties of platinum as a contact material for igniting combustible gas, **Perl** (U. S. Patent 615,363, Dec. 6, 1898) states that after the discovery that finely-divided platinum did not fulfil the requirements, the endeavor was made to increase the effect of the finely-divided platinum by mingling the same with different porous bodies, according to the suggestion of Liebig (Pogg. Ann., Vol. 17 (1829), 107). Dobereiner (Journ. Praktischer Chemie, 1839, Vol. 17, 158) went further and prepared finely-divided platinum within the pores of natural or artificial meerschaum or clay. Perl regards a method of this character to bring about the formation of chloride of magnesium or other earths, because by reduction of the platinum salts which are in the pores of the employed material a part of the latter is always transformed by the action of the acids freed from the platinum salts (chiefly hydrochloric acid) into compounds which are injurious on account of their hygroscopic properties, and which act as fluxes, causing the igniting material to become denser and more impenetrable for the gas after a short time. To meet these objections Perl proceeds as follows:

Porous combustible material is thoroughly mingled with a solid or dissolved platinum salt. The mixture is dried at a moderate temperature. and the platinum

* U. S. Patent 1,077,442, Nov. 4, 1913.

is reduced in the pores of the incombustible material by bringing the mixture to a high degree of heat in a covered crucible until the hydrochloric acid or the vapors of any other acid have disappeared. The same result is also brought about by heating the mixture in a reducing gas flame. The residual salts are now extracted with diluted hydrochloric acid and subsequently with water until all trace of any soluble salts removed.

Efrem (British Patent 14,339, 1899; J. S. C. I., 1900, 726) and Chem. Fab. vorm. Goldenberg (British Patent 618, 1900; J. S. C. I., 1901, 250) employ clay and similar supporting material for platinum in preparing catalytic material. (See also British Patents 6448, 1905; J. S. C. I., 1906, 432 and 10,729, 1901; J. S. C. I., 1902, 548.)

C. E. Munroe (U. S. Patent 724,317, March 31, 1903) produces a form of platinum contact material active in oxidation processes by causing the formation upon perforated sheets or disks of asbestos and upon sheets or disks of perforated metal or woven wire of a coating of finely-divided platinum. For instance, a perforated sheet of asbestos is immersed in an alcoholic solution of ammonium chloride and then in an alcoholic solution of platinic chloride, or, if preferred, the sheet may be first immersed in the platinic chloride and subsequently in the ammonium chloride, forming upon the surface of the asbestos a crystalline precipitate of ammonium-platinic chloride. When the precipitate has been formed, the sheet of asbestos is heated. The heat acts first to drive off the alcohol and then decomposes the double platinum salt, leaving the metal in a very finely-divided state.

Paal and **Amberger** * describe the production of preparations of a greasy consistency containing inorganic metal colloids of the platinum group, consisting in incorporating solutions of the divalent salts of the metals of the platinum group with bodies maintaining colloids in the colloidal state (protecting colloids) especially with wool fat or the alcohols obtainable therefrom by saponification, and adding a carbonate of an alkali to form the colloidal lower hydroxides of the metals employed. They note that preparations containing combinations of the divalent salts of the metals of the platinum group in a colloidal condition can be obtained, if, instead of the alkali carbonates used above, the alkali salts of certain weak organic acids are selected, for instance, the salts of the higher, saturated, or unsaturated, fatty acids (soaps). In this way there are produced in the presence of solutions of the metal salts, for instance, of divalent palladium, or platinum, triturated with wool fat, products which contain the corresponding palladium, or platinum, salts dissolved in colloidal form in the wool fat.

If, according to Paal and Amberger, wool fat be impregnated with a concentrated aqueous solution of palladious chloride ($PdCl_2$) and the mass be then triturated with the equivalent quantity of potassium oleate in concentrated aqueous solution, the salts mutually decompose with formation of potassium chloride and palladious oleate which remains dissolved in colloidal form in the wool fat. As the palladious chloride is difficultly soluble in pure water but readily in hydrochloric acid it is dis-

* U. S. Patent 1,077,891, Nov. 4, 1913.

solved in the latter and the acid is neutralized before triturating the liquid with wool fat by means of an amount of sodium carbonate equivalent to the hydrochloric acid used. The neutral $PdCl_2$ then remains dissolved in the liquid.

In order to obtain a preparation containing about 25 per cent colloidal palladious oleate 0.85 part of palladious chloride $PdCl_2$ = 0.5 part of palladium are dissolved with the application of heat in 0.45 part of fuming hydrochloric acid (38 per cent HCl) and 2 parts of water, and the hydrochloric acid is neutralized by the addition of 0.3 part of anhydrous soda either solid or dissolved in 0.7 part of water. The solution of $PdCl_2$ thus obtained is then triturated intimately in small portions with 9.5 parts of wool fat softened at a gentle heat. Into the body thus obtained are then stirred, also in small portions, 3.5 parts of potassium oleate dissolved in 15 parts of water. The formation of the palladium oleate is detected by the fact that the greasy mass colored red-brown by the palladious chloride becomes, on being triturated with the potassium oleate, first yellow-brown, then gray-brown and, after being allowed to stand some considerable time, black-brown. To purify the product it may be either treated repeatedly with hot water at from 50° to 60° C., and the mass exposed in vacuo at from 40° to 50° C., for the purpose of removing the water; or the original product may be dissolved in from 5 to 6 times its volume of petroleum ether of low boiling point, the greater part of the by-products remaining undissolved and the red-brown liquid organosol being dried with calcium chloride or dehydrated sodium sulfate. In this case a further part of the by-products separates along with the water. The petroleum ether is then distilled off from the liquid freed from the drying agent. The colloidal palladium oleate can be enriched in the "ointment" body by solution in petroleum ether and precipitation with alcohol. A product is thus obtained containing about 70 per cent of colloidal palladium oleate, which like the 25 per cent preparation, is absorbed as organosol by all organic substances dissolving wool fat. Instead of a palladious salt, a platinous or other salt of the platinum group can be used, for instance, the salt of divalent platinum resulting from the reduction of the platinochloride-hydrochloric acid with sulfur dioxide. Wool fat impregnated with platinous salt, when acted on by an aqueous solution of potassium oleate, forms a colloidal platinous oleate $(C_{18}H_{33}O_2)_2Pt$. A mixture of the wool fat alcohols obtained from wool fat by saponification can be used in the same manner as wool fat. The wool fat alcohols are in their properties very similar to the wool fat itself and the mixture of alcohols obtained therefrom by saponification presents a still greater affinity for water than wool fat. The wool fat alcohols have a more solid consistency than the wool fat.*

Meyer † reports an experiment on the hydrogenation of olive oil with a colloidal palladium hydroxide solution containing 0.2 gram

* Amberger (Kolloid-Zeit. (1913), **13**, 310) has prepared organosols of palladium, platinum, palladious hydroxide, palladium oleate and platinous hydroxide. In the preparation of the metallic organosols, hydrazine hydrate was used as a reducing agent. The palladium organosols (8 : 9 to 16 per cent Pd) had pronounced catalytic activity; small quantities dissolved in fatty oils were capable of transferring hydrogen to the unsaturated glycerides of the oil, with the formation of so-called hardened oils. The platinum organosols contained 8.14 to 18.4 per cent Pt. The hydroxide organosols were prepared by the interaction of the corresponding chlorides and sodium carbonate and the palladium oleate organosols from the chloride and potassium oleate in presence of wool fat. (J. S. C. I. (1914), 41.)

† Dissertation, Karlsruhe, 1912.

palladium and 0.34 gram gum arabic in 100 cc. Two volumes of olive oil to one volume of the colloidal solution were heated and agitated in an autoclave at a temperature of 70° to 80° C. under a hydrogen pressure of 6 atmospheres. Hydrogen was added to replace that absorbed. After one-half hour no further absorption of hydrogen could be noted, but the agitation was continued for 2 hours. The fat was then separated from the colloidal solution and boiled with water. A solid fatty product was obtained.

For the purpose of combining hydrogen with nitrogen to make ammonia the Badische Anilin & Soda Fabrik * recommend cerium and a " promoter " as a catalytic agent.

With some exceptions, compounds of the alkali metals and the alkaline earth metals are said to act as promoters of the catalytic power. Also oxides of the rare earth metals, tantalum and niobium, as well as silica, may be employed as promoters. As a general rule those metals or compounds of the metals which yield oxides and salts which are non-reducible by hydrogen are suitable for use as promoters. On the other hand, the metalloids, such for instance as sulfur, selenium, tellurium, arsenic, phosphorus, and also the easily fusible and easily reducible metals, such for instance as lead, tin and zinc, generally act as contact poisons, whether the element be added or be present as such or in the form of a compound.

The following example is given. Take metallic cerium which has been prepared electrolytically and is in the condition of small grains, and mix it with about two per cent of its weight of powdered potassium nitrate, and then place the mixture in the contact tube. On passing a mixture of hydrogen and nitrogen through the tube, while heating, a catalytic agent is obtained which is said to give about three times the yield that the untreated cerium affords.

* U. S. Patent 1,068,968, July 29, 1913.

CHAPTER VII

THE OCCLUSION OF HYDROGEN AND THE MECHANISM OF HYDROGEN ADDITION

As an acquaintance with the subject of hydrogen addition and reduction by hydrogen of various bodies may lead to a broader knowledge of catalytic reactions in the hydrogenation of oils, the following notes by various observers are included.

Sieverts and Krumhaar* did not find hydrogen to be absorbed by the metals cadmium, thallium, zinc, lead, bismuth, tin, antimony, silver and gold. The solubility in copper, nickel, iron and palladium is shown in the graphic curve diagram. (Fig. 50.)

The curves show that the solubility increased regularly with the temperature up to the melting point and then suddenly increased, the solubility in the liquid metal then increasing regularly in the same manner. With palladium, however, the solubility was independent of the temperature up to the melting point and then diminished to one-half, and in the liquid metal was again independent of the temperature. On cooling, copper retained 20 per cent and nickel 8 per cent of the hydrogen absorbed, and in the case of iron, the evolution of gas was so violent on solidification that the tube was blown to pieces, leaving a spongy regulus. In experiments with alloys it was found that the addition of gold lowered the solubility of oxygen in silver. The copper alloys and hydrogen formed three groups: (*a*) those in which the solubility was not influenced, such as silver; (*b*) those in which the solubility was lowered, such as gold, tin, aluminium; (*c*) those in which the solubility was higher than that accounted for by the copper content, such as nickel and platinum. The solubility in copper alloys was proportional to the square root of the pressure, and the view that occlusion was due to adsorption is untenable, and although Sieverts and Krumhaar hold the view that adsorption did not exist at high temperatures, they do not express any opinion about low temperature conditions, and they put forward the view that gases and metals form solid and liquid alloys, the solubility of which does not follow Henry's law, but is expressed by the formula $\frac{\sqrt{P}}{m}$.

Exhaustive data are given by Sieverts (Z. physik. Chem. (1911), 591) of the solubilities of hydrogen in the three metals, copper, iron and nickel, at pressures up to 1.5 atmospheres, and temperatures from 400° to 1600° C. It is shown in the case of nickel that the amount of gas absorbed by the metal under given conditions of temperature and pressure is independent of the amount of metallic surface. The hydrogen-containing metals are therefore true solutions. At constant temperature the solubility both in solid and liquid metals is proportional to the square root of the gas pressure, the quotient $\frac{\sqrt{\quad}}{\quad}$ (where m is the mass of gas absorbed by 100 grams

* Berichte (1910), **43**, 893.

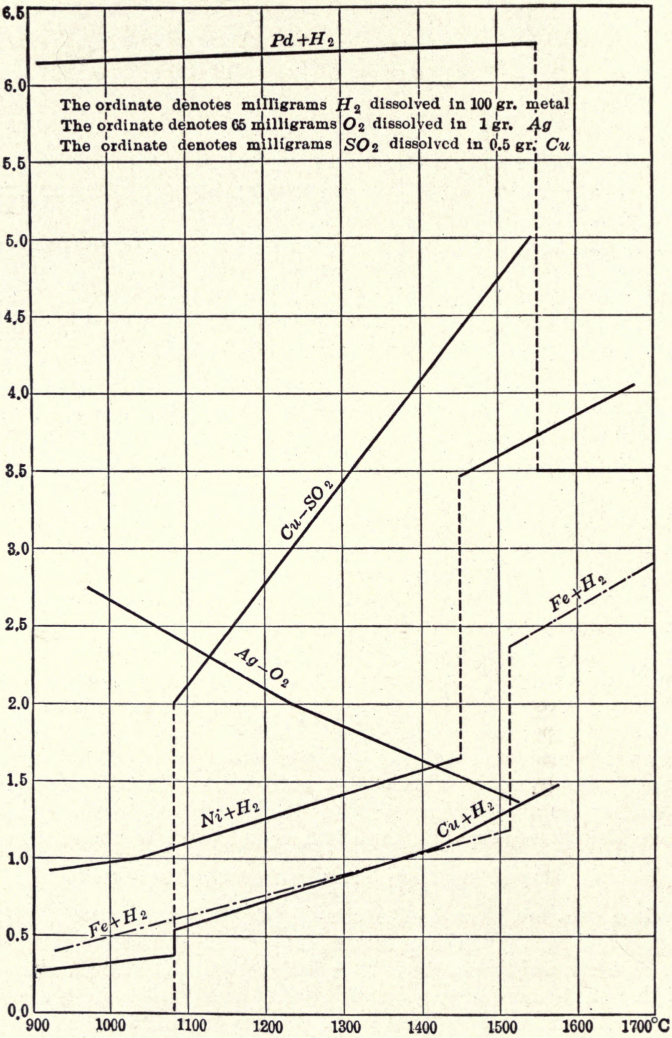

Pd + H₂
The ordinate denotes milligrams H₂ dissolved in 100 gr. metal
The ordinate denotes 65 milligrams O₂ dissolved in 1 gr. Ag
The ordinate denotes milligrams SO₂ dissolved in 0.5 gr. Cu
Cu–SO₂
Ag–O₂
Fe+H₂
Ni+H₂
Cu+H₂
Fe+H₂
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
900
1000
1100
1200
1300
1400
1500
1600
1700°C

FIG. 50.

of metal) being remarkably constant for values of p above 10 mm. At constant pressure the solubility increases with temperature, and shows a sudden increase at the melting points of all three metals. The transition from β to γ iron is also marked by a rapid increase in solubility between 850° and 900° C. This discontinuity though very marked is not so sudden as that at the melting point. The transition from a to β iron is not accompanied by any change in solubility. In the liquid metals the solubility continues to increase with rise of temperature, probably more rapidly than in the solid state. On solidifying in an atmosphere of hydrogen all three metals "spit." Copper gives off about twice its volume of hydrogen (at 1084° C. and 760 mm.) iron about 7 times its volume (at 1510° C. and 760 mm.) and nickel about 12 times its volume (at 1450° C. and 760 mm.). The regulus contains cavities in which hydrogen may be retained. It is only, however, after very rapid cooling that any considerable quantity of the absorbed hydrogen can be retained at ordinary temperatures.

With regard to the occlusion of hydrogen by various metals, the following table is instructive.* The numbers indicate the volumes of hydrogen under normal conditions absorbed by one volume of the metal.

Silver wire	0.21
Silver powder	0.91–0.95
Sheet aluminum	1.1–2.7
Reduced cobalt	59–153
Copper wire	0.3
Reduced copper	0.6–4.8
Iron wire	0.46
Cast iron	0.57–0.8
Reduced iron	9.4–19.2
Magnesium	1.4
Reduced nickel	17–18
Gold leaf	0.48
Precipitated gold	37–46
Molten lead	0.11–0.15
Zinc	Traces

From a study of the action of nickel and hydrogen on various hydrocarbons at different temperatures, the following conclusions are drawn by **Padoa** and **Fabris** †: (1) In the dehydrogenation of monocyclic and polycyclic hydrogenized hydrocarbons, gaseous hydrocarbons are formed to some extent. If a hydrocarbon yields several hydrogenation products, the most highly hydrogenized one is most readily decomposed in this manner. Of the hydrocarbons examined, tetra- and di-hydrophenanthrene yielded no hydrocarbon decomposition

* Abegg and Auerbach, Hdb. d. Anorganischen Chemie Vol. II, part I, 55.

† J. S. C. I. (1908), 1083.

products even under increased pressure, and tetrahydronaphthalene did not under atmospheric pressure.

(2) The decomposing action of nickel is influenced by pressure.

For instance, at atmospheric pressure, tetrahydronaphthalene is simply dehydrogenized with liberation of hydrogen, whereas under a pressure of 3 atmospheres, gaseous hydrocarbons are formed. (3) The several hydrogenation products of a hydrocarbon can each be obtained from the most highly hydrogenized product by the action of nickel at a definite temperature, but it is not possible to effect a gradual progressive splitting off of hydrogen. In almost all cases dehydrogenation begins at a higher temperature than hydrogenation. Under atmospheric pressure hydrogenation and dehydrogenation are distinct processes; in most cases nickel can effect either reaction, but on certain compounds, the nickel acts only in one way. Under increased pressure, the two limits of temperature, viz., the highest at which hydrogenation is possible and the lowest at which dehydrogenation takes place, are closer together, and under certain conditions, the two processes may proceed simultaneously until equilibrium is attained.

Relative to its behavior to hydrogen, **Holt, Edgar** and **Firth** * state that palladium may exist either in an active or a passive state, the former rapidly taking up hydrogen, the latter being practically inert. Heating to a temperature of 400 degrees in hydrogen and cooling renders the palladium very active. New palladium may be made active by the repeated oxidation and reduction of the surface. The activity diminishes gradually on standing, but may be restored on heating.

When spongy palladium was exposed to hydrogen at temperatures from −50° C. upwards, Gutbier (Ber. (1913), 1453) found that the amount of occluded gas steadily decreased from −50° C. (917 volumes to 1 of palladium) to a minimum at 20° C. (661 : 1) then slowly rose to 105° C. (754 : 1). The hydrogenized palladium was pyrophoric.

It is suggested that the activity is due to the presence of a metastable modification of the palladium which gradually reverts to a more stable variety at ordinary temperature. Measurements have been made of the rate of sorption (this term includes both adsorption and absorption) of hydrogen by palladium free from hydrogen, and palladium containing varying amounts of previously-sorbed hydrogen. No marked difference was observed between the action of moist and dry hydrogen. With palladium containing little or no hydrogen the rate of sorption first increases rapidly and then slowly diminishes. On the other hand, if the palladium has already sorbed considerable quantities of hydrogen the initial increase is not observed. It would appear that when active palladium is exposed to an atmosphere of hydrogen there is first a rapid condensation (adsorption) of the gas at the surface, probably in the form of complex molecules, forming a layer of high vapor pressure. This is

* Z. physik. Chem., 82, 513.

followed by a slow diffusion (absorption) into the interior of the metal. This would explain the rapid rise in pressure followed by slow increase observed when palladium partially saturated with hydrogen is exposed to a vacuum. The sorption is accompanied by evolution of heat. Measurements were also made of the rate of diffusion of hydrogen through a palladium tube. The rate is found to increase with rise in temperature, but it is also influenced by the state of the metal. This accounts for the fact that the same diffusion velocity is not always found at the same temperature. It is very doubtful that the hydrogen sorbed by the palladium is at the same concentration throughout the metal, even after long standing.

The rate of absorption of hydrogen by limonene in the presence of platinum black has been studied by Vavon (Comp. rend. (1914), **158**, 410), and two stages or phases of the reaction were noted. The velocity curves for the absorption of hydrogen have a gradient which varies considerably with the quantity of catalyst present. Apparently the metal can become fatigued so that while it is active enough to bring about the easier stages of hydrogen addition, it is not powerful enough to effect the more difficult stages of saturation. This is more marked after the catalyst has been heated to a temperature of 300° C. or higher, when the activity can be varied and suited to bring about hydrogenation in a selective and regular manner. When heated above 500° C. platinum black is transformed into an inactive modification.

The work of Andrew and Holt (Proc. Roy. Soc. (1913), A. **89**, 170), which leads to the conclusion that palladium is dimorphic, is discussed by Halla (Z. physik. Chem. (1914), **86**, 496), who shows that palladium black prepared by Graham's method is not inactive. He also shows that occlusion by active palladium is not hindered at ordinary temperatures by contact with the inactive metal.

Mixtures of hydrogen and oxygen combine with explosion on contact with platinum or carbon which has been heated to a temperature sufficient to cause the emission of electrically-charged particles from the surfaces of platinum or carbon. If platinum is exposed to Roentgen rays which cause the emission of charged particles an explosion may be brought about without heating the platinum. (J. R. Thompson, Chem. Ztg., Rep. (1914), 15.)

Investigations directed towards an explanation of the precise nature of hydrogen transfer by means of the platinum metals are not lacking. Wieland* assumes that palladium hydride, or for that matter any metal hydride, unites as such with the unsaturated compound at the double bond and that the labile addition product breaks down, with retention of the hydrogen and elimination of palladium, the latter being then in condition to take up additional hydrogen and again form an addition product. From a thermodynamic standpoint the hydrogenation process appears to be a reversible reaction. In the case of ethylene compounds, and in fact, in general, the reaction is exothermic, but is endothermic in the case of the double bonding of the aromatic series. Thus the metal addition product would appear in the reaction equilibrium as follows:

$$-R=R- + PdH_2 \rightleftarrows \begin{array}{cc} -R & -R- \\ H & PdH \end{array} \rightleftarrows \begin{array}{cc} -R & -R- \\ H & H \end{array} + Pd$$

* Ber., 45, 484.

In this connection it may be stated that Skita and associates have isolated an addition product of palladium chloride with an unsaturated body but work along this line has not been extensive and the explanation advanced that catalyzers simply split the hydrogen molecule to yield hydrogen in an atomic or nascent condition is for the present perhaps as satisfactory as any.*

Troost and Hautefeuille† believed that their experiments vindicated the formation of a definite compound Pd_2H, while Dewar‡ suggested the existence of Pd_3H_2. The experiments of Hoitsema§ indicate that between 20 and 200 degrees no definite compounds of palladium and hydrogen exist.

Sabatier‖ considers nickel catalysis to be due to the formation of hydrides. First hydrogen acts on the metal, quickly forming a compound in the superficial layers of the latter. The hydride which results becomes decomposed, and in the presence of bodies which are capable of hydrogen addition, union with the hydrogen takes place. The metal is regenerated and the rôle endlessly repeated.

The variations in activity of nickel which have been noted probably depend on the formation of different hydrides. Thus, for example, well-prepared nickel catalyzer may form the perhydride NiH_2 which is sufficiently active to hydrogenate benzol. Nickel prepared at high temperatures, or if slightly poisoned, may form the lower hydride

$$\begin{array}{c}\mathrm{NiH}\\ \|\\ \mathrm{NiH}\end{array}$$

which is not active on benzol but which is catalytic for olefines and nitro compounds.

Were this assumption correct it would appear as a consequence that nickel and the other active metals (copper, iron, cobalt and platinum) not only should effect a union of hydrogen, but also that hydrogen-containing compounds should suffer removal of their combined hydro-

* Some experimental work of Paal (Ber., 45, 2221) is of interest. Paal notes that apparently only those compounds with two C : C groups in which these groups are separated by at least one carbon atom can be catalytically reduced stepwise. Thus PhCH : CHCH : CHAc in alcohol with colloidal palladium and two hydrogen equivalents give about 50 per cent each of the original ketone and of the fully reduced compound $(PhCH_2)$ Ac. Similar results were obtained with PhCH : CHCH : $C(CO_2H)_2$, piperinic acid and piperine. Phorone, on the other hand, yields almost quantitatively dihydrophorone, Me_2CHCH_2COCH : CMe_2, b. 176 degrees; semicarbazone, needles, m. p. 133 to 134 degrees. (Chem. Abs.)

† Comp. rend., (1874), **78**, 686.

‡ Chem. News, (1897), **76**, 274.

§ Zeit. phy. Chemie (1895), 1.

‖ Die Hydrierung durch Katalyse, Leipsic (1913), 17.

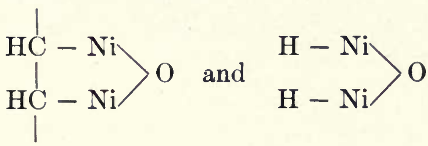
gen, the metals acting as dehydrogenating catalyzers. This actually proves to be the case. Between 250° to 300° C. finely-divided copper readily acts as a dehydrogenating catalyst, converting primary alcohols to aldehydes and secondary alcohols to ketones, in fact affording a very advantageous method for bringing about these transformations.

Results obtained by hydrogenation with nickel. The results obtained by hydrogenation with reduced nickel are classed by Sabatier into 4 groups:

1. Simple reduction without the fixation of hydrogen.
2. Reduction effected simultaneously with the fixation of hydrogen.
3. Fixation of hydrogen by addition to the molecules where multiple bonds exist.
4. Hydrogenation effected with the decomposition of the molecule.

The well-established impossibility of effecting all these changes with *any* metal leads Sabatier to think that for nickel there exists many degrees of combination with hydrogen. Nickel obtained by the reduction of the chloride, as well as that reduced at a temperature above 400° C. is, without doubt, able to produce only a primary hydride, analogous to that of copper and capable of acting on nitro groups or on the double ethylene bond. Only " healthy " nickel, such as that produced by the reduction at a low temperature of the oxide obtained from the nitrate, is able to form a perhydride capable of hydrogenating the aromatic ring.

In the case of nickel oxide catalyzers Erdmann indicates that the transference of hydrogen probably takes place in one of two ways: either an intermediate phase represented by the compounds



or a decomposition of water may take place in accordance with the reaction:

$$Ni_2O + H_2O = 2\,NiO + H_2$$

yielding hydrogen in a nascent state which is assumed to unite with the unsaturated fat while the nickel oxide formed is reduced to the suboxide by hydrogen in the molecular condition.

In an experiment conducted by **Mayer** and **Altmayer*** nickel, reduced from the oxide by hydrogen, was introduced into a Jena glass vessel in an electric furnace, and after complete exhaustion, known

* Berichte (1908), 41, 3062.

quantities of hydrogen were introduced, and the temperature kept constant until absorption ceased. The amount absorbed, at temperatures of 360° to 560° C., was at each temperature proportional to the pressure of the hydrogen. At 360° C. 1 volume of nickel absorbed 50.5 volumes of hydrogen at a pressure of 300 mm., whilst at 560° C. the same absorption occurred when the pressure was raised to 440 mm. Within the experimental limits, then, the system nickel-hydrogen is bivariant, the volume absorbed being dependent both on temperature and on pressure.

Amorphous palladium absorbs hydrogen far more rapidly than the crystalline form, but holds it only feebly. The amorphous form also takes up hydrogen and transmits it to the crystalline variety, so that crystalline palladium coated with the amorphous metal will absorb hydrogen much more rapidly than when uncoated.*

Adsorption is quite variously regarded by various authorities as one of the following: (1) True chemical combination. (2) True solid solution. (3) A modified solid solution in which practically only the outer layers become saturated owing to the difficulty of diffusion in solids. (4) Condensation on the outside of the surface of the solid. According to **McBain** † the first three are contrary to the requirements of thermodynamic theory, and the fundamental assumption of the third is disproved by experiments involving the time required for adsorption of hydrogen. The fourth is found insufficient to explain the somewhat complex time relationships studied here, which, however, point strikingly to the conclusion that both true solid solution (true diffusion) and surface condensation occur. They are independent of each other and their relative importance and magnitude depend upon the conditions of the experiment.

The non-committal name "sorption" is coined to designate the sum total of the phenomena, while "absorption" and "adsorption" are restricted to the dissolved and superficially-condensed matter respectively. It is found that the surface condensation requires only a few minutes for completion, whereas absorption requires, in the case of hydrogen diffusing into carbon at the temperature of liquid air, a dozen hours for practical completion. Thus it was possible to isolate the two phenomena and to study them more or less independently of each other. For instance, by suitable manipulation a sample of carbon can be prepared highly charged with hydrogen in a state of solid solution but almost destitute of occluded hydrogen condensed on the surface. This is clearly attainable (if the hypothesis be correct) by suddenly exposing to a vacuum carbon which has been previously saturated by long contact with hydrogen at a constant temperature. Such carbon, exposed to a low pressure of hydrogen and cut off from all external influences, took up hydrogen

* Proc. Roy. Soc., London (A), 89, 170–186, Chem. Abs. (1914), 457.

† Seventh Int. Cong. Appl. Chem., 1909.

at first (surface condensation) although already supersaturated (i.e., in respect to the solid solution), and then gave it off again in still greater quantity until final equilibrium was established. Thus the manometer first fell for a few minutes and then rose to a higher point than the initial value. In the converse case, where the interior was saturated by a very short exposure to a high pressure of gas, hydrogen was first given off, and then taken up again by diffusion into carbon. Here the manometer automatically rose for a few minutes, then steadily fell for many hours to a lower value than previously obtained. The pressure changes observed might at first seem unimportant, were it not for the one fact of great significance, viz., that (taking the second case just outlined) the higher pressure at five minutes was even less than corresponded to the gas condensed on the surface of the carbon, yet after a dozen hours had elapsed a much lower pressure was attained, a pressure which then actually did correspond to the condensed gas in equilibrium with it. Thus a considerable body of hydrogen had been transferred from the surface to the interior of the carbon. An approximate calculation of the extent of this transfer showed that the true solubility of hydrogen at the temperature of liquid air and under 2 cm. pressure was at least 4 c.c. (corr.) per gram of the cocoanut carbon employed. This absorption was roughly proportional to the square root of the pressure (whereas the total sorption varies as the cube root of the pressure). From this it appears that the dissolved hydrogen is split up into single atoms.

Tomassi * considers that the reductions caused by hydrogen at the moment of its liberation from its compounds are wrongly attributed to its being in an allotropic condition,† such as is usually connoted by the term "nascent"; for, in that case, he argues, the same reactions ought always to follow whatever the origin of the gas; but this is not borne out by experiment.

Thus, silver chloride, bromide or iodide, suspended in water acidulated with sulfuric acid, can be reduced by the hydrogen liberated from water by electrolysis, but show no signs of reduction when the water is decomposed with sodium amalgam. Or, if a solution of potassium chlorate be acidulated with sulfuric acid, and zinc added, the chlorate is reduced to chloride; whereas if sodium amalgam be added, no reduction takes place. Nor does sodium amalgam bring about the reduction of chloric acid or of the chlorates of sodium, barium, copper, lead or mercury. In the case of potassium perchlorate, none of the usual reducing agents have any effect; zinc or magnesium with sulfuric acid, or zinc with potash or soda, or in a boiling solution of copper sulfate, all failing to bring about reduction, but, on the other hand, this is readily effected by sodium hydrosulfite — a compound from which hydrogen is not liberated. Similarly, a solution of nickel sulfate, to which potash and potassium cyanide have been added, acquires a reddish tint on the addition of zinc, while hydrogen is liberated; but if magnesium, or a magnesium-platinum couple, replace the zinc, the red color is no longer produced, although hydrogen is still liberated. Kern found (Bull. Soc. Chim., 26, 338) that by the action of magnesium on ferric chloride, ferric hydroxide was produced, and this fact Tomassi confirms, with the addition that he obtains the same result by using sodium amalgam

* Monit. Scient., 1898 [51], 182.

† It has been suggested by Osann that active or occluded hydrogen is in an allotropic form comparable to ozone.

instead of magnesium. According to Stahlschmidt, nascent hydrogen derived from the decomposition of water by zinc dust reduces potassium nitrate to nitrite, reduced iodides and iodates, but does not reduce chlorates; and De Wilde has established the fact that sodium amalgam reduces potassium bromate, but is without action on the chlorate.

On these and similar facts Tomassi bases his opinion that the reducing power of nascent hydrogen varies according to the chemical reaction by which the hydrogen was produced, and he considers that if the gas has a greater affinity in the nascent than in the ordinary condition, this is entirely due to the hydrogen at the moment of its liberation from a compound being accompanied by the heat produced during the liberation. Hence, if nascent hydrogen be represented by the symbol $H + a$ (in which a denotes this amount of heat), the value of a would vary with each chemical reaction, and, as a general rule, the reducing power of nascent hydrogen would be proportional to that value, provided that the reaction between the hydrogen and the substance to be reduced could once be started. There are certain cases, however, in which the reduction is due, not to the hydrogen, but to the metal which served to generate it. The reduction of potassium chlorate by means of sulfuric acid and zinc, or by electrolysis of its solution with a zinc anode, is an instance of this. If such a solution be electrolyzed with both electrodes of platinum, oxidation occurs at the anode, with the formation of perchlorate, while no trace of chloride is found at the cathode; but if a zinc anode be used, chloride is formed at the anode, but not at the cathode. From this Tomassi concluded that the reduction in this case must be attributed, not to the hydrogen, but to the zinc uniting with the oxygen of the chlorate in accordance with the equation $KClO_3 + 3\,Zn = KCl + 3\,ZnO$.

Titoff * has studied the adsorption of hydrogen and other gases by pure gas-free cocoanut charcoal. The temperature varied from − 79° to + 151.5° C., and the pressures from 0 to 77 cm. of mercury. The results are given in tables and the relations illustrated by isothermal and isobaric curves. Hydrogen appears to obey Henry's law for a considerable range of temperature (− 80° to + 80° C.). Titoff prefers a surface condensation theory as an explanation of the phenomena, and consequently he uses the term adsorption, rather than absorption, which would seem to suggest ordinary solution.†

Firth observes that the adsorption of hydrogen (surface condensation) by wood charcoal occupies only a few minutes, while the equilibrium due to absorption is attained only after several hours, hence "sorption" is of a two-fold character. Wood charcoal contains crystalline as well as amorphous carbon and the activity of the material depends chiefly on the latter.‡

* Z. physik. Chem. (1910), 74, 641; see also Homfray, J. S. C. I. 1910, 1055.

† Rhead and Wheeler (Chem. Soc. Proc. (1913), 29, 51) observe that carbon, at all temperatures up to 900° C. and probably above that temperature, has the power of pertinaciously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but may be expelled by increasing the temperature of the carbon during exhaustion. When quickly released in this manner, it appears, not as oxygen, but as carbon dioxide and carbon monoxide.

‡ Z. physik. Chem. (1914), 294; J. S. C. I. 1914, 130.

The presence of kaolin favors the combination of hydrogen and oxygen at temperatures from 230 degrees and upwards. Without the kaolin, combination does not take place until a temperature of 350 degrees or higher is reached. The activity of the kaolin depends greatly upon the temperature to which it has previously been heated, and the extent to which it has lost its water of constitution. The lower the water content, the less pronounced is the activity.*

It has been stated by **Marie** † and **Petersen** ‡ that, in the electrolytic reduction of unsaturated acids, the nature of the cathode used has no appreciable influence upon the course and velocity of the reaction. Fokin § finds, however, that reduction can only be effected with cathodes of palladium, platinum, rhodium, ruthenium, iridium, osmium, nickel cobalt and copper, and that the quantity and the physical condition of the metal has a considerable influence on the course of the reduction. It is shown that the metals named have the capacity of occluding hydrogen, with the formation of unstable hydrides. It is these metals, also, which have been found to act as hydrogen-carriers in the reduction processes studied by Sabatier and Senderens. Fokin is of the opinion that all reduction processes taking place in presence of the metals mentioned, viz., electrolytic reduction, reduction of gaseous substances by reduced metals by the process of Sabatier and Senderens, reduction by galvanic couples, and reduction by metal hydrides in solutions, are due to a special activity of the occluded hydrogen, probably owing to such hydrogen being in the monatomic condition. The activity of the metals varies directly with their capacity of occluding hydrogen; palladium is the most efficient, and then follow, in the order given, platinum, nickel, cobalt and copper. Fokin has studied in this way the reduction of the fatty acids from linseed oil, Japanese wood oil, castor oil, cod-liver oil, and other unsaturated acids.

According to Fokin the metals can be grouped into those which, like palladium and cobalt, form definite hydrides; and those which, like platinum and nickel, have not been proved to form such definite hydrides. The latter class gives the best results in reduction catalyses.‖ By the action of excess of cobalt hydride at 270° C., under atmospheric pressure, oleic acid is reduced to stearic acid to the extent

* J. S. C. I. 1914, 254, and Comp. rend. (1914), **158**, 501.

† Compt. rend., 136, 1331; J. S. C. I. 1903, 1003.

‡ Z. Elecktrochem., 11, 549; J. S. C. I. 1905, 895.

§ J. russ. phys. chem. Ges. (1906), **38**, 419; Chem. Centr. (1906), **2**, 758; J. S. C. I. 1906, 935.

‖ Zeitsch. f. ang. Chem. (1909), **22**, 1451–1459 and 1492–1502.

of 26 to 28 per cent, while in a sealed tube, the reduction proceeds to the extent of 60 per cent. If an ethereal solution of oleic acid be treated with palladium black, and a current of hydrogen led through, stearic acid can be detected after one-half hour; with platinum black under similar conditions, 24 per cent of stearic acid is obtained after one-half hour, 84.5 per cent after $3\frac{1}{2}$ hours and 90 per cent after 5 hours. Oleic acid is also reduced by nickel and cobalt (prepared from the oxides), in presence of hydrogen, at temperatures of 45° to 184° C. and 98° to 250° C. respectively.*

In order to test the view that the increased reducing power of occluded hydrogen is due to a kind of physical compression, **Fokin** carried out a series of experiments, which showed that compressed hydrogen (up to a pressure of 35 atmospheres) effected the reduction of unsaturated hydrocarbons more rapidly and completely and at lower temperatures than hydrogen at atmospheric pressure.†

Hydrogen reduces certain metals from their solutions, as, for instance, silver from an aqueous solution of the nitrate. The action of hydrogen on metallic solutions is much more energetic when one operates under pressure as has been observed by Beketoff.

In connection with the effect of hydrogen on metallic catalysts to alter the properties of the metal, a discussion appearing in the Metallurgical and Chemical Engineering (1913), 679, on the "Passivity of Metals," is of interest. According to Foerster and also Schmidt a metal such as iron is passive in its normal condition and only becomes active under the influence of a catalyst. Hydrogen is stated to have this catalytic effect and hydrogen ions have also the same action. Schmidt states that the most important of the catalysts which overcome the passive state of metals is hydrogen and that a small amount of it can activate large amounts of iron, nickel and chromium. The preparation of a non-pyrophoric catalyzer of the nickel type by passing carbon dioxide or similar gas over it for a considerable period may perhaps depend on the elimination of the hydrogen which permits the metal to resume its normal passive state, in which condition exposure to the air does not injure the catalytic activity.

Towards hydrogen, palladium in sheet form appears to be both active and passive. In the active form the metal will rapidly absorb large amounts of the gas, while in the passive condition only slight amounts are occluded. The absorption of hydrogen proceeds in two stages; first, a rapid occlusion at the surface and second, a slow absorption into the metal mass.‡

* J. S. C. I. 1907, 1149.
† J. S. C. I. 1907, 169.
‡ Zeitsch. phys. Chem. (1913), 513.

CHAPTER VIII

THE ANALYTICAL CONSTANTS OF HYDROGENATED OILS*

The hydrogenation of oils has to such an extent changed certain of the constants by which oils and fats are at least in part identified, namely, the iodine number and the specific gravity, that the identification of a fat or fatty mixtures, often heretofore a troublesome matter at best, now promises to become even more difficult.

The reduction of the iodine number through the introduction of hydrogen into the oil, in a sense, is arbitrary; there is no difficulty in reducing the iodine number almost to zero through the hydrogenation process, or at any moment to interrupt the operation and from one and the same initial material to produce products having the most varied iodine numbers.

The specific gravity and melting point advance hand in hand as saturation progresses, the specific gravity approaching that of tristearin, while the resultant melting point in considerable measure depends upon the molecular weight and the hydroxyl content of the fatty acid components of the oil. The specific gravity of a hardened cottonseed oil whose iodine number had been reduced to zero was found by **Normann and Hugel** † to be 0.9999 at 15° C., while they note that tristearin has a specific gravity of 1.0101 at the same temperature.‡

The index of refraction also is strongly modified. A sample of fish oil at 56° C., according to Normann and Hugel, showed a figure of 53.8; while after hardening to an iodine number of 22.5 the index was 36° C. at the same temperature. (Scale of the Zeiss butter refractometer.)

Observations made in the author's laboratory on the index of refraction of a number of hydrogenated oils gave the results noted below:§

* Jour. Ind. Eng. Chem. (1914), 117.

† Chem. Ztg. (1913), 815.

‡ The specific gravity of tristearin is given by the Chemiker Kalender as 1.0101 at 15° C., while Lewkowitsch reports the specific gravity of a specimen of not quite pure stearin in the melted state as 0.9235 at 65.5° C.

§ A sample of hydrogenated cottonseed oil used extensively in this country exhibited a refractive index of 1.4492 and a melting point of 59.9° C.

INDEX OF REFRACTION AT 55° C.

(Abbé Refractometer *)

	Original oil	Hydrogenated oil
Corn	1.4615	1.4514 (M. P. 55.7° C.)
Whale (No. 1)	1.4603	1.4550 (M. P. 41.5° C.)
Soya bean	1.4617	1.4538 (M. P. 50.3° C.)
Cocoanut oil ("olein")	1.4429	1.4425 (M. P. 24.7° C.)
Linseed	1.4730	1.4610 (M. P. 42.3° C.)
Palm	1.4523	1.4517 (M. P. 38.7° C.)
Palm	1.4523	1.4494 (M. P. 44.8° C.)
Peanut (edible)	1.4567	1.4547 (M. P. 34.7° C.)

It is of interest to note that while the addition of *hydrogen* to fatty oils reduces the index of refraction, the addition of *oxygen* increases the index as is shown in the case of blown or ozonized oils.

The gradual reduction of the index of refraction by progressive hydrogenation is shown in the following table compiled from determinations made in the author's laboratory.

Cottonseed oil was hydrogenated for a period of ten hours and samples were drawn at one-hour intervals.

	Melting point	Index of refraction, 55° C.
Original oil	....	1.4588
1 hour	28.2° C.	1.4577
2 hours	31.3	1.4568
3 hours	34.3	1.4557
4 hours	37.9	1.4549
5 hours	40.8	1.4540
6 hours	43.8	1.4527
7 hours	45.6	1.4518
8 hours	47.3	1.4510
10 hours	55.9	1.4496

The saponification number practically does not change. The content of free fatty acids changes but little. A sample of cottonseed oil containing 1.8 per cent fatty acid was found, after hardening to various degrees, to have a fatty acid content ranging from 1.4 per cent to 1.9 per cent. With sesame oil containing 2.44 per cent fatty acid the resulting hardened oil contained 2.55 per cent of acid. The content of unsaponifiable bodies does not essentially change. Cottonseed oil having 0.55 per cent unsaponifiable matter, after hardening,

* Refraction values are given in terms of true refractive index and also according to the arbitrary scale of the butyro refractometer, in order to follow the data available, as rendered.

showed a content of unsaponifiable bodies ranging from 0.45 per cent to 0.55 per cent; sesame oil with an unsaponifiable content of 0.70 per cent, after hardening, contained 0.85 per cent unsaponifiable.

Cholesterol and phytosterol, according to **Bomer,** are not changed by treating oils with hydrogen, although this is somewhat contrary to the statement of Windaus,* according to whom cholesterol may be easily reduced by the catalytic process. **Willstätter** and **Mayer** † hydrogenated cholesterol in ether solution with a platinum catalyzer.

An examination of the unsaponifiable constituents of several hardened oils has been made by **Marcusson** and **Meyerheim** ‡ who used the digitonin method for the separation of sterol. The following table gives the results obtained.

UNSAPONIFIABLE CONSTITUENTS OF HARDENED OILS

	Total unsaponifiable matter		Sterol obtained by digitonin method	Sterol-free unsaponifiable components		
	Per cent	$[\alpha]_D$	Per cent	Per cent	$[\alpha]_D$	Iodine number
Cottonseed oil (solidifying point 32° C.)	0.7	− 5.8	0.22	0.4	+ 6.8	....
Cottonseed oil (solidifying point 38° C.)	0.6	± 0	0.14	0.4	+ 8.1	....
Linseed oil	1.0	+19.5	0.21	0.7	+19	85
Castor oil	0.3	−10.1	0.13	0.19	+ 5.2	....
Talgol	0.9	− 1.9	0.10	0.7	+ 1.3	56.1
Talgol extra	0.9	− 3.3	0.07	0.7	....	....
Candelite	0.8	+ 4.7	0.05	0.7	+ 4.8	....
Candelite extra	0.7	+ 1.4	0.024	0.64	+ 2.8	....

The examination showed that the sterol content of hardened fats is slightly less than that of the corresponding natural fat or oil. The cottonseed oil first listed was prepared by the Wilbuschewitsch process at 150 to 160° C. with hydrogen under pressure. The second sample of the cottonseed oil was made by the Normann process, presumably at a higher temperature but without pressure. At temperatures of 150 to 160° C. apparently the difficultly reducible sterol is not affected by hydrogen and Marcusson and Meyerheim call attention to the observations of Adamla § who could not hydrogenate cholesterol with a

* Ber. d. chem. Ges. (1912), 3051.

† Willstätter and Mayer converted cholesterol quantitatively into dihydrocholesterol by passing a slow stream of hydrogen for two days through an ethereal solution of cholesterol in the presence of platinum black (Ber., 1908 (41), 2199). (See U. S. Patent to Ellis, 1,086,357, Feb. 10, 1914.)

‡ Zeitsch. f. angew. Chem., 1914, 28, 201.

§ Dissertation. Beiträge zur Kenntnis des Cholesterins, Freiburg, 1911, 12.

nickel catalyzer at temperatures below 170° C. Marcusson and Meyerheim found cholesterol to hydrogenate readily at 195° C. while phytosterol was practically unchanged after treatment with hydrogen at 200° C. From these and other tests it was found that cholesterol is much less resistant than phytosterol to the action of hydrogen.

The content of sterol decreases with increasing melting point as shown by the following table.

Hydrogenated oil	Iodine number	Solidifying point	Sterol content
Whale oil (not hydrogenated)	114	....	0.13
Talgol	67	31	0.10
Talgol extra	36	38	0.07
Candelite	20	42	0.05
Candelite extra	13	45	0.02

The unsaponifiable constituents of hardened fat when freed from sterols were of light yellow color and of salve-like consistency. These sterol-free bodies obtained from Talgol, Talgol extra, Candelite and Candelite extra, when recrystallized from benzine, yielded a product melting between 59.3° and 59.8°, which proved to be a fatty alcohol, probably octodecyl alcohol.

In the case of the acetyl number more noticeable changes take place according to **Normann** and **Hugel.** When hardening castor oil, for example, the hydroxyl number in one sample dropped from 156 to 102; in another sample the number fell to 131. The hydroxyl group is thus more or less broken down by the hydrogenation process, at least under some conditions of treatment.

HYDROGENATED CASTOR OIL

Acid number	3.5
Saponification number	183.5
Iodine number	4.8
Acetyl number	153.5
Acetyl number of the fatty acids	143.1
Acid number of the fatty acids	184.5
Saponification number of the fatty acids	187.9
Melting point of the fat	68° C.
Melting point of the fatty acids	70° C.
Melting point of the acetylated acids	47° C.

The properties of hardened castor oil have been noted by **Garth** * whose observations differ somewhat from those of Normann and Hugel. As is generally known, castor oil differs materially from many

* Seifen. Ztg. (1912), 1309.

other common oils in such respects as its high viscosity, solubility in alcohol and difficulty of salting out its soaps by electrolytes. Hardened castor oil dissolves in alcohol only by heating and separates on cooling, but is soluble at ordinary temperature in chloroform. The constants of one sample of hardened castor oil examined by Garth are given in the above table.

These results obtained by Garth would indicate that the saponification and acetyl number do not change. The iodine number has fallen greatly and the melting point is much increased. The difference between the acid number of the fatty acids and their saponification number points to the formation of lactones. As is known castor oil has the property at high temperatures of forming anhydrides, accompanied by polymerization.

The effect of hydrogenation on color tests of oils is variable. Thus the **Boudouin** sesame oil test is not influenced; in fact the reaction seemingly is sharper after treatment of the oil with hydrogen, while the **Halphen** test is not likely to give positive results even with oils which have been only slightly hardened.

The **Becci** test is operative with slightly-hardened cottonseed oil, but is indistinct with highly-hardened oil so that this test is significant only in event of a positive coloration.

Hardened fish oil loses all its essential characteristics, such as the formation of well-defined bromine compounds of the higher unsaturated fatty acids. Thus there are obtained after hardening, new fatty acids corresponding to the saturated bodies, arachidic ($C_{20}H_{40}O_2$) and behenic ($C_{22}H_{44}O_2$) acids, which in variable amounts up to a proportion of 20 per cent and more have been observed in certain hydrogenated oils. In the hardening of rape oil behenic acid is formed from the erucic acid present. Other oils or fats with a noticeable proportion of acids with more than 18 carbon atoms in the molecule apparently scarcely ever come into the trade.

The complete conversion of erucic acid to behenic acid is readily obtained by reducing with hydrogen in the presence of nickel. This method has been used by **Lewkowitsch** in the determination of erucic acid.*

The saturated fatty acids obtained by the hydrogenation of the unsaturated acids of Japanese sardine oil were found by **Majima** and **Okada** † to have a melting point of 75° C. and a molecular weight of 349, and consisted in the main of the higher homologues of stearic acid, such as $C_{20}H_{40}O_2$ or $C_{22}H_{44}O_2$. Similar results were obtained on

* Lewkowitsch, Oils, Fats and Waxes, 5th edition, Vol. I, 195 and 553.

† J. S. C. I., 1914, 362.

hydrogenating the more fluid fatty acids obtained by chilling and pressing.

As a test for hydrogenated peanut oil, **Kreiss** and **Roth*** have given a method which consists in saponifying 20 grams of the oil with 40 cc. of alcoholic potash; then adding 60 cc. of alcohol and acidifying by the addition of 50 per cent acetic acid of which approximately 15 cc. are required. One and one-half grams of lead acetate are added and the mixture allowed to stand overnight. The lead salts which separate are decomposed by boiling with 5 per cent hydrochloric acid, the fatty acids are dissolved in 50 cc. of 90 per cent alcohol with slight warming and the solution is placed in water at 15 degrees for about one-half hour. The crystals which separate are recrystallized from 25 cc., then $12\frac{1}{2}$ cc. of 90 per cent alcohol and the melting point determined. The presence of at least 5 per cent arachidic acid causes the melting point of the third crystallization to be over 70° C.

Normann and **Hugel**† state that this test is applicable likewise to hardened fish and rape oil. They tested a number of samples of fish oil from several sources and found in each case that the melting point of the recrystallized fatty acids was at least 70 degrees. Normann and Hugel also state that it is unnecessary with hardened fish oil to allow the lead acetate to react for several hours, it sufficing simply to let the mixture stand until cooled to room temperature; this can be hastened by cooling with water. So large a proportion of fatty acids is obtained according to this procedure that the specified amount of alcohol is not sufficient to dissolve them. It is better to use 100 to 150 cc. of alcohol and heat on the water bath until solution is affected. The application of heat should not be continued for any great length of time as arachidic acid readily forms esters. The mixture is then placed in cold water, cooled to room temperature and the separated material collected and crystallized several times from alcohol used in progressively diminishing proportions. Three crystallizations suffice for only slightly hardened fats. With fats of higher consistency one must recrystallize several times more until the melting point is constant.

In one case using hardened fish oil having a melting point of 44, three recrystallizations from alcohol gave a constant melting point of only 63 degrees, while further recrystallization using acetone caused the melting point to advance to 76 degrees. In doubtful cases one should try several solvent mediums. If the melting point is found to be above 70° C. Normann and Hugel think it proof that either hardened fish, rape or peanut oil is present. If one is certain of the unitary

* Chem. Ztg. (1913), 58 and 369.

† Ibid. (1913), 815.

character of the oil then peanut and rape oil can be distinguished from fish oil by the cholesterol test, provided the statement of Bomer in regard to the unchangeability of cholesterol and phytosterol under ordinary conditions of oil hydrogenation is confirmed.

Data on hardened oils by Davidsohn* are tabulated below:

	M. P.	Acid number	Saponification number	Moisture	Ash
Talgol	39.3	3.4	191.0	0.10	0.07
Talgol extra	46.5	3.5	191.3	0.13	0.05
Candelite	49.0	3.2	191.0	0.20	0.08
Candelite extra	51.9	3.9	190.8	0.15	0.04
Coryphol	79.3	3.3	189.9	0.18	0.05

These hardened fish oils or other hardened oils put out under the trade names indicated are manufactured by the Germania Oil Works of Emmerich.

Knapp† states that the attention of analysts should be directed to the fact that in the immediate future they will be called upon to analyze certain new artificial fats prepared by hydrogenation and, not improbably, to detect their presence as adulterants. Thus, for example, starting with olive oil, as the absorption of hydrogen proceeds, a turbid oil, then a liquid magma, then a soft fat and finally a hard fat is obtained. Knapp observes, " A similar change occurs with all oils containing glycerides of unsaturated acids. This rise in the melting point is naturally accompanied by a decrease in the iodine value and refractive index. Fats have been prepared in this way from cottonseed oil with iodine values as low as 5, and if desired the iodine value could doubtless be reduced to 0, and the melting point raised to 60° or 70° C. While it is too costly for commercial purposes to carry the saturation of the unsaturated glycerides to completion, it might be of value in the laboratory as an aid to determining the component glycerides in a pure oil. Not only the oils containing glycerides of oleic acid can be hardened, but also those containing glycerides of linolic acid and linoleic acid (the drying oils), and even of such highly unsaturated acids as clupanodonic (in whale oils). Anyone who has seen a malodorous oil converted into a bland odorless tallow realizes the commercial possibilities of the process. And when it is remembered that the process can be stopped when the iodine value reaches a desired number, the possibility becomes evident of the preparation

* Org. f. d. Ol- und Fetthdl. (1913), Nos. 14 and 15, and Seifen. Ztg. (1913), 529.
† The Analyst (1913), 102.

of a fat with any required analytical figures." In support of the foregoing, **Knapp** furnishes the following data:

Appearance	Original oil. Clear liquid	Hardened oils		
		Solid particles floating	Soft greasy solid	Brittle solid
Butyro-refractometer (corrected to 40° C.)	57.7	....	....	47.7
Fatty acids:				
Iodine value	110	94	55	22
Titer	34.7° C.	37.0° C.	42.5° C.	52.2° C.
Neutralization value: (mg. KOH)	197	196	196	192

The analyst is chiefly interested in the question of how these fats are to be detected. It is doubtful if their most characteristic feature, the relatively high percentage of stearic glycerides which they contain, will be of much service. Knapp states that until the manufacturer accomplishes the difficult step of completely removing the nickel, the detection of traces of this metal will be the simplest and most reliable test for hardened oils.* Although the catalyst is very finely divided, the manufacturer can obtain a perfectly clear fat by careful filtration, and hence it is the nickel contained in the nickel soaps formed by the free fatty acids present that one has to detect. The following method is suggested: 50 grams of the fat are heated in a flask with 20 cc. hydrochloric acid, with continued vigorous shaking. The mixture is allowed to separate while hot, and part of the acid solution is evaporated to dryness, dissolved in a drop of water and placed on a white tile. One drop of ammonium sulfide is added to this and also to a drop of water for comparison. Knapp, however, tried this test only on a few hardened oils, and in some cases with negative results. Dimethylglyoxime is a much more delicate test, but unfortunately **Prall** has found† that certain pure untreated oils give a red coloration. Hence further investigation is needed.

One of the most characteristic tests for fish oils — the bromide estimation — is quantitatively useless for these oils after hardening,

* Too much reliance should not be placed on the nickel test as evidencing the presence or absence of hydrogenated oils. It is known to the writer that hardened oils which are free from nickel are on the market, these in some cases presumably having been prepared with the aid of palladium as a catalyzer.

† Bomer, Zeitsch. Untersuch. Nahr. Genussn, (1912), 24, 104, and Analyst (1912), 37, 452.

as the percentage of ether-insoluble brominated glycerides is greatly reduced thereby. Not only are the analytical figures for the oils altered by this absorption of hydrogen, but also the traces of substances which often serve as a useful test for the particular oil in which they occur — e.g., Halphen's reaction. Knapp believes Bomer's observation that phytosterol and cholesterol are not changed in this process is of great analytical value.

Three fats obtained by Knapp from a clear cottonseed oil, hardened by hydrogen with the help of different catalysts, gave the following figures:

Catalyst	Percentage of catalyst	Character of product	Butyro-refraction (Corrected to 40° C.)	Melting point, °C.
Nickel	1.00	Hard	45.7	49
Platinum	1.10	Hard	47.8	46
Palladium	0.06	Brittle	45.5	52

The keeping properties of these hardened oils were found to be remarkably good. Although prepared nearly a year and a half previously and having often been exposed to damp air, yet they showed no signs of rancidity. The free acidity (0.70 per cent as oleic acid) did not appreciably change during the period of observation.

Bomer* is in substantial agreement with the foregoing, for he states that (1) the hardened oils, as a result of the more or less complete transformation of unsaturated fatty acids (oleic, linoleic, linolenic) into stearic acid, show an increase in the melting and solidifying points as well as a lowering of the refractometer number and iodine number while the saponification number is but little altered.

(2) Judging by the iodine numbers of the liquid fatty acids, these acids appear to be not uniformly transformed into stearic acid, but the transformation of oleic acid appears to progress more slowly than the less saturated linoleic and linolenic acids, etc.†

(3) Among the hardened oils, the soft and medium-hard products, in color, consistency and in part also in odor and taste show a greater or less similarity to beef or mutton tallow, so that by external appear-

* Chem. Rev. u. d. Fett und Harz Ind. (1912), 220.

† Muller (Seifen. Ztg. (1913), 1376) examined a hydrogenated fish or whale oil known as Talgit, having an iodine number of 49, and found the iodine number of the liquid fatty acids obtained from this material to be 100, from which he concludes that the addition of hydrogen occurs simultaneously with both the oleic and the more unsaturated acids and not successively in such a manner as to convert the acids containing two or more double bonds into oleic acid before oleic becomes transformed into stearic acid.

ance one cannot distinguish these hardened oils from such animal fats; for example medium-hard peanut oil is so completely like neutral lard, and hardened whale oil is so like mutton tallow, that one is not able to distinguish between these fats by appearance, consistency, odor or taste.

(4) Not only in their outward properties are these hardened oils like hog fat and mutton tallow, but also the usual analytical constants are so similar that one cannot distinguish some samples of hardened peanut oils and hardened sesame oil from hog fat, nor whale oil, in some cases, from mutton or beef tallow. In the latter case even the Polenske numbers agree while in the case of sesame oil they are somewhat lower than hog fat.

Oil	Appearance	Melting point	Solidifying point	Refractometer at 40°	Acid No.*	Saponification No.	Iodine No.
Peanut oil untreated	Yellow liquid	....	....	56.8	1.1	191.1	84.4
Peanut oil hardened	White tallowy	51.2	36.5	50.1	1.0	188.7	47.4
Sesame oil hardened	White tallowy	62.1	45.3	38.4†	4.7	188.9	25.4
Cottonseed oil hardened	Yellowish lard like	38.5	25.4	53.8	0.6	195.7	69.7
Cocoanut oil untreated	White soft	25.6	20.4	37.4	0.3	255.6	11.8
Cocoanut oil hardened	White lard like	44.5	27.7	35.9	0.4	254.1	1.0
Whale oil hardened	Yellowish tallowy	45.4	33.7	49.1	1.1	193.0	46.8

* Milligrams potassium hydroxide for 1 gram fat. † Determined at 50° C.

Bomer examined a number of hydrogenated oils and tabulated the results of his investigations and from these the above condensed table has been compiled.

The solid and liquid fatty acids separated from the hydrogenated fat by the method of Farnsteiner showed the following properties:

Oil	Solid fatty acids		Liquid fatty acids	
	M. P.	Acid No.	Refraction at 40° C.	Iodine No.
Peanut oil untreated	....	....	47.6	91.8
Peanut oil hardened	....	199.7	42.9	82.9
Sesame oil hardened	56.4	199.5	44.7	88.9
Cottonseed oil hardened	45.0	206.8	48.3	115.6
Whale oil hardened	....	199.5	44.4	96.0

Samples of these hardened oils were examined for cholesterol and phytosterol. Hardened peanut oil was found to contain 0.4 per cent, sesame oil 1.9 per cent, cottonseed oil 1.6 per cent and whale oil 0.2 per cent of sterol, of which the three first-mentioned hardened products exhibited the typical crystalline form of phytosterol. The melting point of these sterols ranged from 132° to 139° C., yielding acetates melting between about 126° and 129° C. The hardened whale oil gave a sterol melting at 149.7° C.

Bomer made a series of fractional crystallizations of hardened oil and from a sample of hydrogenated peanut oil obtained tristearin (amounting to about $\frac{2}{3}$ per cent). Bomer has called attention to the rather striking behavior of cocoanut oil. He calculated from the iodine number that the natural oil contained 13 per cent of oleic acid and after hydrogenation approximately about 1 per cent of this acid was present. As a result of the transformation of 12 per cent of oleic acid into stearic acid, the melting point increased from 25.6° to 44.5° C., or thus 18.9° C., while the solidifying point advanced from 20.4° to 27.7° C., or only 7.3° C.

Bomer * has studied the melting points of hydrogenated oils and as regards hydrogenated peanut and sesame oil he notes that the melting points of the least soluble glycerides are very high, being 70.6° C. and 71.5° C. respectively, while the corresponding fatty acids melted at 68.6° C. and 68.5° C.; hence these glycerides apparently consist of tristearin. The hydrogenated cottonseed oil examined yielded a mixture of glycerides of melting point 61.3° C. and derived fatty acids melting at 38° C.

A species of hardened fish or whale oil, known as "Talgit," has been examined by **Müller** † who found the product to have an acid value of 12.8, an iodine number of 49 and a titer (fatty acids) of 39.4° C. The fat was saponified and pressed to obtain stearic acid. It was found that the operation of pressing could be carried out effectively to yield a product technically free from liquid fatty acids; 35 per cent of solid fatty acid having a titer of 48.7° C. was thus obtained. Müller states that since mixtures of stearic and palmitic acids possess a solidifying point above 53.5° C. the low titer of the solid acids of Talgit points to the presence of solid acids other than stearic and palmitic. Dubovitz ‡ thinks the low melting point to be due to the presence in the original fish or whale oil of hypogaeic and physetoleic acid or similar acids with possibly unsaturated fatty acids of a still lower number of carbon atoms.

* Z. Untersuch. Nahr. Genussm. 1914, 153; J. S. C. I., 1914, 323.

† Seifen. Ztg. (1913), 1376.

‡ Ibid. (1913), 1445.

Leimdorfer* regards the stearin produced by the hydrogenation of some oils to be perhaps an allotropic form of natural stearin.

The hydrogenation of linseed, peanut and sesame oil, using nickel oxide as a catalyzer, according to **Bedford** and **Erdmann**, affords approximately pure stearic glyceride.†

An attempt is made by **Grimme**‡ to identify fish oils after they have been hardened. As stated, the ordinary constants give no clue to the original source of a hardened oil and hence Grimme resorts to color reactions. A list of tests is given for each of the four classes of fish oils: (1) Seal oils; (2) Whale oils; (3) Liver oils; (4) Fish oils; and also characteristic tests for individual oils. These tests were also applied to two hardened oils of unknown origin and Grimme believes from his results that the color reactions are characteristic enough to establish the presence of fish oils. Nickel was found in the samples, Fortini's test (as detailed below) giving the strongest coloration. Color reactions were applied to six authentic whale oils from two different sources, and hardened to different degrees. These tests were carried out by dissolving 5 parts of the sample in 95 parts of benzine-xylene (1 : 1) and agitating 5 cc. of the solution with the reagent; after 5 minutes and 60 minutes the color was noted. Grimme finds the iodine-sulfuric acid reaction (1 cc. concentrated sulfuric acid and 1 drop tincture of iodine) to give a characteristic violet-red color for whale oil though the intensity of coloration decreases with increasing hardness. The constants of the six samples of hydrogenated fish and whale oils employed and the coloration produced by different reagents are tabulated by Grimme.

CONSTANTS OF HYDROGENATED FISH AND WHALE OILS

Sample	Consistency	Specific gravity	Melting point	Solidifying point	Index of refraction	Acid No.	Acid No. as free oleic acid, %	Saponification No.	Iodine No. (Wijs)
			°C.	°C.					
I	Lard like	0.9256	38.5	32.8	1.4569	3.72	1.91	188.8	56.76
II	Tallowy	0.9259	40.0	35.2	1.4548	8.49	4.26	189.8	49.82
III	Tallowy	0.9258	42.4	36.4	1.4543	5.64	2.90	189.6	41.36
IV	Tallowy	0.9263	44.8	39.3	1.4539	4.39	2.21	189.2	35.71
V	Tallowy	0.9271	47.2	41.5	1.4536	4.40	2.25	188.7	26.95
VI	Tallowy	0.9271	48.0	42.0	1.4530	2.18	1.10	189.3	23.18

* Ibid. (1913), 1317.
† Jour. f. prakt. Chem., 1913, 432.
‡ Chem. Rev. u. d. Fett und Harz Ind. (1913), 129 and 155.

COLOR REACTIONS (GRIMME)

Reagent	Color of layers	I	II	III	IV	V	VI
1 cc. conc. sulfuric acid	Acid	Brown	Cherry red	Cherry red	Yellow	Yellow	Yellow
	Fat solution	Yellow	Yellow	Light yellow	Light yellow	Colorless	Colorless
1 cc. 70 per cent sulfuric acid	Acid	Light brown	Light brown	Light brown	Yellow	Yellow	Yellow
	Fat solution	...	...	...	...	...	...
1 cc. 20 per cent sulfuric acid	Acid	Rose	Rose	Light rose	Light rose	Faint rose	Colorless
	Fat solution	...	...	...	...	...	...
1 cc. acetic anhydride, then 10 drops of conc. sulfuric acid	Acid	Dark brown	Brown	Brown	Brown	Light brown	Light brown
	Fat solution	Grayish green	Grayish green	Grayish green	Grayish yellow	Grayish yellow	Grayish yellow
1 cc. mixture equal parts conc. sulfuric acid and fuming nitric acid	Acid	Red brown	Red brown	Brown	Brown	Light brown	Light brown
	Fat solution	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
Diluted with water after ½ hour	Acid	...	...	...	...	...	...
	Fat solution	Yellow	Yellow	Bright yellow	Bright yellow	Bright yellow	Bright yellow
5 drops conc. sulfuric acid saturated in the cold with bichromate; after 5 minutes 5 cc. water	Acid	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
	Fat solution	Brownish black	Brown	Brown	Brown	Brown	Brown
10 drops fuming nitric acid	Emulsion	Brownish red	Brownish red	Brownish red	Brownish red	Brownish red	Brownish red
Diluted with water after ½ hour	Acid	...	...	...	...	...	...
	Fat solution	Light brown then yellow	Light brown then yellow	Light brown then yellow	Yellow	Yellow	Yellow
10 drops aqua regia	Acid	...	...	...	...	...	...
	Fat solution	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow
Diluted with water after ½ hour	Acid	...	...	...	...	...	...
	Fat solution	Brownish-yellow	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow
1 cc. conc. sulfuric acid and one drop tincture of iodine	Acid	...	...	...	...	...	...
	Fat solution	Violet red	Violet red	Violet red	Violet red	Violet red	Violet red

A draft of the **Codex alimentarius Austriacus,** which has been prepared by a board of prominent chemists and officials including Hefter, Wolfbauer, Fischer, Hartl and Pellischek,* embraces the subject of hydrogenated oils and it is stated that considered as a food product these oils will require further careful investigation before it is determined with certainty just what rank they will take as edible products. It is noted that the fats now offered for edible purposes are white to yellowish in color, almost odorless and tasteless. Usually the consistency lies between that of ordinary butter and hard tallow. Now and then samples are found which melt at about 60° C. and are as brittle as carnauba wax. These hard products, of course, are not intended by themselves to be used for edible purposes, but are employed to raise the melting point of soft fats. Samples of hardened peanut and sesame oil with iodine numbers reduced to 50 or lower, sometimes down to 20, have been examined. Cocoanut oil with an iodine number of 2 or even lower has been met with. The cholesterol of animal fats and the phytosterol of vegetable oils are not altered by the hydrogenation process. The hardened fats, it is stated, scarcely ever appear on the market in their true light, but usually are put out under some trade name such as "Peanut-oleo," "Sesame-oleo," "Peanut-margarine," "Sesame-margarine," "Crisca," and the like.

Hardened oils examined by **Aufrecht** † in outward appearances resembled palm kernel oil. They were very hard and of granular fracture, were either pure white or yellowish in color. A distant odor was perceptible on melting or heating. The taste recalled that of tallowy fats. The products were readily soluble in the usual fat solvent mediums, but the solubility in methyl and ethyl alcohol was very slight. The fats were easily saponifiable. The content of free fatty acid fluctuated between 0.51 to 0.83 per cent. The ash reacted alkaline and consisted of alkali carbonate and traces of iron oxide, but no nickel or other constituent could be detected. The analytical results are given in table on the following page.

The detection of traces of nickel by the usual analytical methods is often difficult.‡ Dimethylglyoxime, proposed by **Tchugaeff,** is a reagent of great sensitiveness. Its application has been investigated by a number of chemists, and among these Bianchi and Di Nola § report that the presence of copper and iron interferes with the test. They worked with an acid reagent and used the following procedure:

* Seifen. Ztg. (1913), 1087.

† Pharm. Ztg. (1912), 876.

‡ Methods of determination are given by Grossmann, Die Bestimmungmethoden des Nickels und Kobalts, Stuttgart, 1913.

§ Boll. Chim. Farm. (1910), 517.

To the substance supposed to contain nickel one or two drops of concentrated hydrochloric or nitric acid are added and the acid solution so obtained is placed in a porcelain dish, or preferably on a strip of filter paper. A few drops of ammonia are added, or in case the strip of filter paper is used, this may simply be exposed to the vapors of ammonia. The liquid is acidified with acetic acid and a drop of concentrated alcoholic solution of dimethylgloxime is added. The presence of nickel is shown by a red coloration which grows more pronounced in the course of time. This reaction is a very simple one and does not require any particular technical knowledge for carrying out.

	1 Durotol (yellow)	2 Durotol (white)	3 Hydrogenated train oil
Color	Yellowish	White	White
Specific gravity at 15° C.	0.9252	0.9257	0.9268
Melting point, °C.	46.5	46.0	48.0
Solidification point, °C.	43.5	43.5	45.5
Viscosity at 50° C.	5.4	5.4	5.6
Acid No. (calculated as oleic acid)	0.51	0.57	0.83
Saponification No.	162.2	161.0	173.5
Unsaponifiable matter (per cent)	1.92	2.1	2.4
Acetyl No.	1.2	1.2	0.95
Iodine No.	3.9	4.2	7.8
Hehner No.	95.8	95.8	96.4
Reichert-Meissl No.	0.38	0.36	0.52
Water	0.0	0.0	0.0
Ash	0.037	0.03	0.05

Fortini * has simplified this reaction and uses an alkaline instead of an acid reagent which apparently gives more satisfactory results than the above procedure. Fortini mixes one-half gram of dimethylglyoxime, 5 cc. 98 per cent alcohol, and 5 cc. concentrated ammonium hydroxide in the order given, yielding a clear, faintly yellowish liquid which in glass-stoppered bottles may be kept for a long time unchanged. The test is carried out as follows:

The sample to be examined is freed from fat by extraction with ether and to the residue a drop of the reagent is added. When nickel is present there will appear in a few seconds a rose-colored flock caused by reaction with the nickel oxide present on the surface of the metallic nickel. Of course, if nickel is present in the form of a soap, the fat should be extracted with, for example, aqueous hydrochloric acid in the manner prescribed by Knapp in the foregoing. In order to make the reaction even more sensitive, the residue may be heated for a few moments in an oxidizing flame to produce nickel oxide.

* Chem. Ztg. (1912), 1461.

Kerr * proposes the following modification of the dimethylglyoxime test for nickel in hydrogenated oils and fats:

Ten grams of the fat to be tested are heated on the steam bath with 10 cc. of hydrochloric acid (specific gravity 1.12), with frequent shaking for 2 to 3 hours. The fat is then removed by filtering through a wet filter paper, the filtrate being received in a white porcelain dish. The filtrate is evaporated to dryness on the steam bath, 2 to 3 cc. of concentrated nitric acid being added, after it has been partly evaporated, to insure the destruction of all organic matter. After the evaporation is complete the residue is dissolved in a few cubic centimeters of distilled water and a few drops of a one per cent solution of dimethylglyoxime in alcohol added. A few drops of dilute ammonia are then added. The presence of nickel is shown by the appearance of the red colored nickel dimethylglyoxime. The amount of nickel present may be estimated by comparing the color developed with that developed in a standard solution of a nickel salt.

The detection and determination of small quantities of nickel by α-benzildioxime is described by **Atack** † as follows:

An alcoholic solution of α-benzildioxime gives with nickel compounds a bulky red precipitate which is insoluble in water, alcohol, acetone, 10 per cent acetic acid and ammonia; the precipitate becomes reddish yellow on boiling. The reagent is much more sensitive than dimethylglyoxime, showing 1 part of nickel in 5 million of water, and the precipitate is readily filtered.‡ Small quantities of nickel are determined as follows: 150 cc. of a hot saturated alcoholic solution of the oxime are added for every 0.01 gram of nickel, the mixture is heated for a few minutes on the water bath, filtered, the precipitate washed with hot alcohol, and dried at 110° to 112° C.; it has the formula $C_{28}H_{22}N_4O_4Ni$ and contains 10.93 per cent Ni. Nickel may be separated from cobalt in ammoniacal solution. α-Benzildioxime is prepared by boiling 10 grams of benzil, dissolved in 50 cc. of methyl alcohol, with a concentrated aqueous solution of 8 grams of hydroxylamine hydrochloride, for 6 hours, washing the precipitate with hot water and then with a small quantity of ethyl alcohol, in which it is only slightly soluble. It may be crystallized from acetone.

According to **Lindt**, nickel may be determined colorimetrically by means of potassium thiocarbonate. Metals of the hydrogen sulfide group and manganese, cobalt and zinc should not be present.§

* Jour. Ind. & Eng. Chem., 1914, 207.
† Chem. Ztg. (1913), 37, 773.
‡ Compare Ibbotson, J. S. C. I. (1911), 1317.
§ J. S. C. I., 1914, 335.

The hydrogen value is proposed by **Fokin*** as a means of determining unsaturated organic compounds in a manner similar to the iodine values of Hubl and Wijs.

The " hydrogen value " of an organic compound is defined as the number of cubic centimeters of hydrogen (at 0 degrees and 760 mm.), which are absorbed by 1 gram of the compound. For the test an apparatus is devised consisting of a distillation flask (50 to 150 cc.) having a small beaker fused inside on the bottom, and connected by means of the side tube to a gas burette and a gasometer containing hydrogen. In the small beaker are placed about 0.1 gram of catalytic platinum, moistened with ½ cc. of water, and in the flask the substance to be examined and 20 to 30 cc. of alcohol free from dissolved oxygen. Hydrogen is admitted and the flask is shaken by a shaking machine until absorption is complete. The following hydrogen values were obtained by Fokin, the figures in parentheses being either the hydrogen values corresponding with Wijs' iodine value, or, where indicated, the theoretical hydrogen values. Elaidic acid, 78.6 to 81.4 (78.8); oleic acid, 86.2 to 87.2 (86.2); fatty acids from sunflower oil, 119.6 to 120.8 (122.9); fatty acids from linseed oil, 164.9 to 166.3 (166.0); castor oil, 73.7 (75.5); croton oil, 260.9 (theoretical, 258.4); undecoic acid, 115.6 (114.1); erucic acid, 39.4 (65.6). Colophony does not absorb hydrogen under the conditions of the test. The " hydrogen value " of course is not a determination as yet of use in the identification of hardened oils, but is noted here because of its incidental interest.

The foregoing embraces most of the information available from published sources on the analytical side of hydrogenated or hardened oils and it is hoped that the very meagerness of the data may serve as a stimulus for abundant investigations tending to clarify the subject and enabling fairly definite procedures to be adopted for the qualitative and quantitative examination of these products.

* J. Russ. Phys. Chem. Soc., 40 (1908), 700; J. Chem. Soc. Abstr., 94 (1908), II, 637.

CHAPTER IX

EDIBLE HYDROGENATED OILS

Since the addition of less than 1 per cent of hydrogen suffices to convert cottonseed oil or other vegetable oils into a fatty body of at least the consistency of lard, it follows that manufacturers of ordinary lard compound (that is to say, a mixture of about 85 to 90 per cent of refined cottonseed oil and 10 to 15 per cent or so of oleo-stearin) have promptly turned their attention to the production of compound by a "self-thickened" cottonseed oil.

The high cost * of oleo-stearin prevailing during recent years makes the method an attractive one and the hydrogenated product from cottonseed oil has the advantage, if properly made, of being very stable in character. Unquestionably, also, the hardening process is destined to increase the demand for cottonseed oil in the manufacture of edible fats.

By the hydrogenation process a lard substitute may be prepared in two ways. The entire oil may be simply hardened to the consistency of lard, care being taken to employ an oil as nearly neutral as possible to prevent excessive solution of catalytic metal, and to avoid a high temperature of treatment so as not to impair the flavor of the product. If the color and flavor are detrimentally affected, resort may be had to a further treatment with fuller's earth followed by steam-vacuum deodorization. The addition of a small amount of cocoanut oil benefits the flavor.

The other method is that of making lard compound which, as indicated above, involves thickening a large proportion of normal oil with a small amount of a relatively-hard hydrogenated product. This may be carried out as follows:

After the oil has been hardened, it is freed of catalyzer and then may be run into tanks containing the requisite amount of deodorized cotton oil (or other edible oil) and if necessary the mixture is further clarified and filter-pressed. With hardened cotton oil of 58 to 60

* Even though there may exist no marked price differential between oleo-stearin and hardened cottonseed oil, yet when, as is the case, millions of pounds of lard compound are made weekly in this country, a reduction in cost of but a small fraction of a cent per pound means an important gross saving.

titer, only 7 to 10 per cent is required to thicken the oil to the consistency of lard, although in hot climates a somewhat larger proportion may be needed.* The mixture is run onto a chill roll to cause rapid solidification and after slight aeration to improve the color

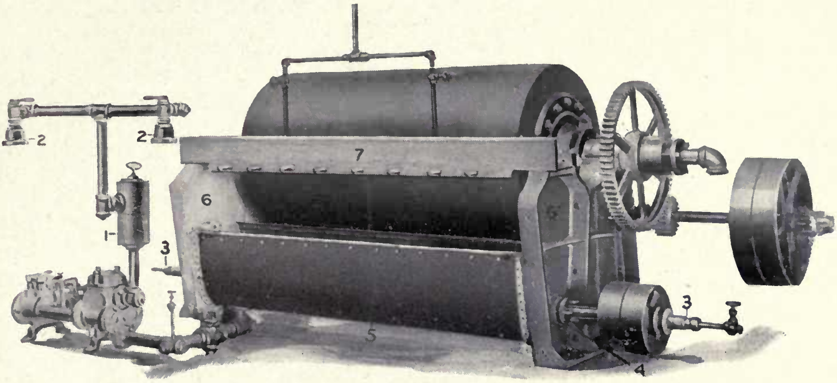


FIG. 51.

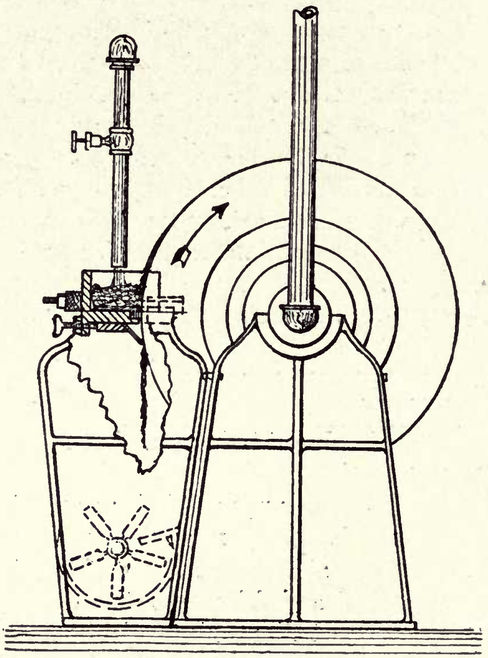
is ready to be packaged. Fig. 51 shows a chill roll or lard cooler of the type usually employed.

In this illustration the large upper cylinder or roll is chilled by the circulation of brine and is slowly rotated say from 6 to 10 r.p.m. The hot liquid compound at a temperature of 50° to 55° C. is run into the feeding trough 7 and falls onto the chilling roll, forming a thin somewhat translucent film which quickly cools and solidifies. The solid fat is removed by a scraper and falls into a picker trough 5. The latter contains a shaft equipped with beating and conveying blades which churn the composition and destroy the translucency, producing an opaque white product of lard-like appearance. The picker is run at a relatively high speed, say 175 to 180 r.p.m. Fig. 52 is an end view showing chill roll, feeding trough and picker. Fig. 53 is an illustration of a modified type of compound cooler. In Fig. 54 the cooler and picker appear on the left hand and in the center is a pump which withdraws the product from the picker and forces it through the pipe line to the packaging cocks on the right hand. Too high a

* The main object to be achieved in making edible and lard compounds is to have them contain as large a percentage of cottonseed oil as possible and yet fulfil the required conditions as to the stiffness of the material to withstand warm temperatures without much softening. Compound which stands a moderately warm climate can be made with even as low as 6 to 7 per cent hardened oil.

speed of the picker blades incorporates an excessive amount of air in the product rendering it "fluffy."*

The speed of rotation of the chilling roll is governed by the rate of feed and temperature of the brine. The latter may be kept between, for example, -5 to $+10°$ F. for good results. If the brine is too cold, the product is liable to drop badly from the roll and the texture



END VIEW.

Fig. 52.

is not always satisfactory. This, however, may be largely remedied by increasing the feed. In winter the brine may be held at a slightly higher temperature to prevent brittleness. In the hottest weather, very cold brine should be used to aid in securing a product which will preserve its color and consistency for a considerable time.

When properly made the compound derived by the hydrogenated oil thickener is excellent in color, texture, flavor and keeping qualities. By many it is considered superior in several respects to oleostearin compound.

* The author desires to make acknowledgment to the Allbright-Nell Co. of Chicago and the Brecht Co. of St. Louis for their courtesy in furnishing the illustrations Figs. 51 to 54.

Possibly, however, for best results as to stability it is desirable to hydrogenate the entire body of oil to a fatty acid titer of 36 or 38, or whatever consistency may be required, rather than to take a relatively small proportion of the oil and harden it to a titer of 50 to 60

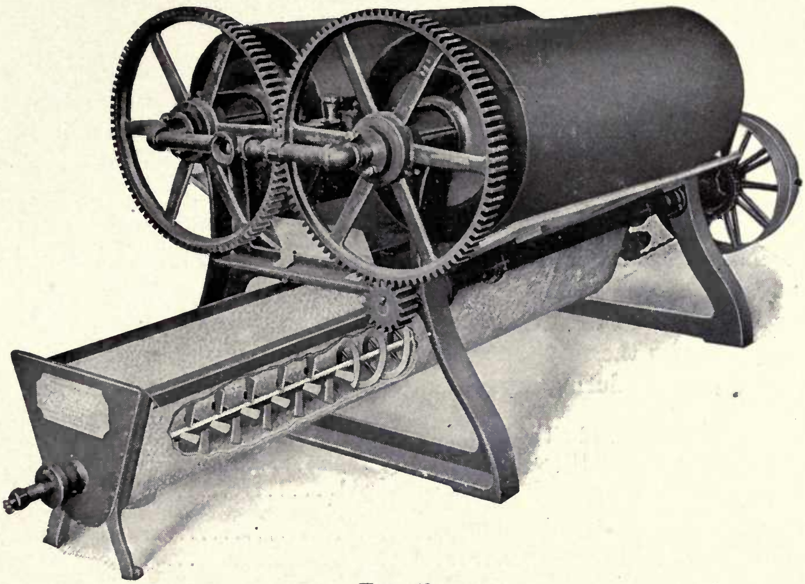


FIG. 53.

or thereabouts and incorporate with unhydrogenated oil. It appears that the hydrogenation of the total body of the oil, by transforming the linoleic and linolenic compounds and the like, has a tendency to improve the oil as regards its edibility and certainly gives it greater stability. The flavor of lard compound is, however, preferred by

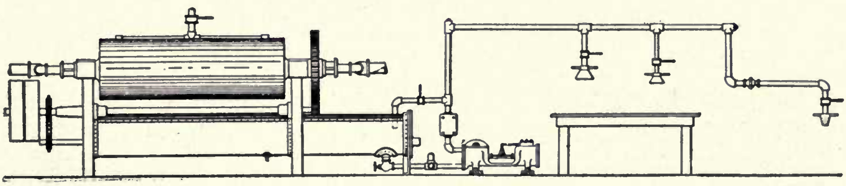


FIG. 54.

many large users of lard substitute presumably because of the proportion of normal oil which it contains, and the manufacturing cost is lower.

Finally, it may be stated, by partial saturation of glycerides, we have the possibility of preparing from tri-olein the oleo-distearin

or the dioleostearin. Dioleopalmitin would give either oleostearopalmitin or distearopalmitin. From tri-olein we may have the two isomeric oleo-distearins, α- and β-oleo-distearin as well as α- and β-dioleostearin. Which of these we may be able to produce controllably and which may prove best from the edible standpoint are problems for the future to solve.

Joslin* calls attention to the economy in using hardened oil "vegetable stearin" in place of oleo-stearin for making lard compound, since only 7 to 10 per cent of the former is called for against 14 to 20 per cent of the oleo-stearin. Of course the amount of hardened oil required depends on its degree of "hardness" but for the present grades of hydrogenated cottonseed oil of 58 to 60 titer, now on the market, the above proportions hold. When the oil is hardened to about the consistency of average oleo-stearin, naturally a greater proportion is needed in lard compound.

Joslin notes the resultant economy by the employment of hardened oil at one plant during a period of one year.

93 parts cottonseed oil at 6.45	$6.00
7 parts hardened oil (vegetable stearin) at 9.25	.65
Cost per hundred pounds of compound	$6.65
86 parts cottonseed oil at 6.45	$5.55
14 parts oleo-stearin at 9.25	1.29
Cost per hundred pounds of compound	$6.84

Or a saving of practically 20 cents per hundred pounds of compound manufactured.

Hydrolecithin has been prepared from lecithin by Riedel.† A hardened fat called "Brebesol" intended for edible purposes is manufactured by the Bremen Besigheimer Ölfabriken.‡

Edibility of Hydrogenated Oils

It seems to be generally accepted by those who have investigated the matter carefully that the hydrogenated oils have as desirable a degree of edibility as the oils from which they are derived. It is even claimed that by destroying traces of certain unsaturated bodies thought to be slightly toxic in nature, hydrogenation renders the oil better adapted for human consumption.

* National Provisioner 1914, 17.

† Method of Preparing Hydrolecithin. German Patent. Compare Paal and Oehme, Ber., 1913, 1297.

‡ Seifen. Ztg., 1914, 263.

A question of serious import has, however, arisen in the use of nickel catalyzer. Aside from the fact that by careless filtration traces of the suspended nickel may be present in the product, there is the more serious problem of the actual solution of nickel to form nickel soaps which cannot be easily removed.

According to **Bomer,*** nickel is dissolved by oils during the hydrogenation treatment only when the oil contains free fatty acid in considerable amounts. A sample of hydrogenated sesame oil containing $2\frac{1}{2}$ per cent of fatty acid was found to contain 0.01 per cent ash with 0.006 per cent nickel oxide. Whale oil, containing 0.6 per cent fatty acid, yielded 0.006 per cent ash and 0.0045 per cent nickel oxide. Such an amount of nickel possibly would be regarded as undesirable or objectionable in a product intended for edible purposes.†

* Zeitsch. Nahr. Genussm. (1912), 104 and Chem. Rev. u. d. Fett. u. Harz. Ind. (1912), 221.

† In a discussion of Bomer's paper (loc. cit.) Lehmann asked whether nickel was found in sufficient amounts to make a quantitative determination in hydrogenated oils, and Bomer replied that the amount of nickel was just so much larger the greater the amount of free acid in the oil and the longer the action of the catalyzer on the oil; while Prall observed that the nickel content of hardened oil depended essentially upon the amount of free acid and that one should reduce the free fatty acid to the lowest possible amount, that with 0.2 per cent free fatty acid in the oil no nickel had been detected in the hardened products examined. One could say, however, that in 100 grams of oil a fraction of a milligram of nickel is detected. Lehmann then remarked that presumably it was to be understood that the presence of nickel could not be avoided and that one-half a milligram of nickel in 100 grams of the oil would be a good result, to which Prall replied that this was the case when the acid of the oil was well removed.

Auerbach (Chem. Ztg., **37**, 297) regards the 0.000002 per cent or so of nickel which remains in hydrogenated oil to be of no practical moment from the standpoint of edibility.

An oil mill in Europe making high-grade peanut oil is now constructing a plant for hardening edible oils by a hydrogenation process that is said to afford a product free from the objectionable traces of nickel found in most of these oils. The hardened oil will be sold to the margarine factories.

Lehmann stated (Bomer, loc. cit.) that we need have no great concern over the utility of this fat or of its physiological action; Straub noted that samples of the hardened oil melted at 53° C. and that fats of such high melting point or in fact any fat melting above 37° C. were not suitable for persons affected with certain maladies of the digestive tract. Lehmann remarked that the work carried on in the Voit laboratory indicated high melting point fats to be injurious, but considering the way hardened fats are made, apparently the means were at hand to make the melting point high or low at will; that fats which were to be eaten must not, of course, have a melting point of 53° C. Bomer added that he was of the opinion that hardened fats were not as beneficial as oil, but that was not the question. The widespread use of edible oils depended on the fact that edible fats must have a certain measure of consistency. Margarine melting at 20 degrees required but a slight addition of

The use of nickel in the form of an oxide, or the use of nickel catalyzer containing a considerable proportion of oxide, is perhaps undesirable from the point of view of solubility in oil. Nickel, in the metallic state, cannot combine with a fatty acid to produce a soap, except with the elimination of hydrogen, and in the presence of an atmosphere wholly of hydrogen, because of mass action, such reaction would not be likely to take place. On the other hand, nickel in the form of oxide would yield water on combining with fatty acid which would be yielded practically into a vacuum as regards the vapor pressure of water. Hence in the manufacture of products intended for edible purposes it is suggested that conditions be maintained such that the catalyzer, if of the nickel type, is preserved almost wholly in the metallic state. Also it is desirable to not force the reaction too rapidly with the consequent danger of breaking down the carboxyl group and setting free water which would react to produce fatty acid.*

a fat melting at 50 degrees. It was not, therefore, a question of the melting point of the hardened oil, but of the melting point of the margarine or other edible fat and the hardened oil was employed simply to adjust the melting point, the same way as beef tallow and the like were used.

A synopsis of Bomer's paper (Z. Nahr. Genussm., 24, 104–113) appearing in Chemical Abstracts, Nov. 10, 1912, 3201, concisely expresses his work. Samples of peanut, sesame, cottonseed and whale oil were hardened. The analyses of the resulting products indicate that the more completely unsaturated fatty acids (oleic, linolenic and linoleic) are converted into stearic with increase in the melting point and the lowering of the iodine number, while the saponification number is scarcely altered. The iodine number of the liquid acids seems to indicate that the less saturated acids are more rapidly converted into stearic than is oleic. The partially saturated products resemble lard in color, taste and odor, while those obtained by further hardening are very similar to beef or mutton tallow. The ordinary constants of the hardened peanut oil are so similar to those for lard that it is very difficult to distinguish it from hog fat, but the phytosterol of the 3 vegetable oils investigated was not affected by the treatment, so that the phytosterol acetate test may be relied upon for the detection of these artificially hardened fats when they are used as adulterants for lard, margarine, etc. Cottonseed oil, after treatment, no longer gives the Halphen reaction, but sesame oil still responds to the Baudouin test. Where nickel is the catalytic agent traces of it will be found in the finished product if there were any appreciable amount of free acid in the original oil. Bomer concludes with a brief report of preliminary work on the stereo-chemistry of the glycerides formed and the requirements which the new product will have to meet to be acceptable as a human food.

* Bouant (La Galvanoplastie (1894), 186) makes the comment that after having considered nickel as dangerous in the preparation of food, it is now recognized, on the contrary, to be harmless. Langbein (Electro Deposition of Metals (1909), 246) observes that hot fats strongly attack nickel. (Trans. Am. Electrochem. Soc., 23, 116 (1913).)

In the course of some investigations by Gates (J. of Phys. Chem. (1911), **15**,

The investigations of various authorities, such as Lehmann, Thoms and Müller have shown that hardened oils used for edible purposes do not cause any derangement of the system and that they are the complete equivalent of animal and vegetable fats of like melting point.* Hydrogenated fats are used just like ordinary fats and do not hinder the assimilation of other food constituents. The nickel content on a daily consumption of 100 grams of the hardened fat is stated to amount at the most to 0.6 mg. and may be regarded as entirely uninjurious. Hardened fat possesses extremely good keeping qualities, and this is probably also the case with margarine prepared from it.† Leimdorfer observes that hydrogenated fats change in odor and color when preserved even in a vacuum.‡

A careful study of the occurrence of nickel in edible products of various kinds has been made by **Normann** and **Hugel.**§ Hardened fats prepared with the aid of nickel catalyzers, and intended for edible purposes, contain traces of nickel which they state amounts to two parts per million. But fats which have been treated in nickel-lined receptacles show fully this content of nickel. Nickel-lined ware has

97) it was observed that many of the common metals are dissolved appreciably by oleic, palmitic and stearic acids, with evolution of hydrogen.

The Bureau of Animal Industry of the Department of Agriculture is investigating the matter and apparently intends to determine the relative degree of toxicity of the traces of nickel in the form existing in improperly made hydrogenated oil. We may add that, so far as can be ascertained, the Department looks kindly upon the advent of hydrogenated oil in view of the likelihood that it is destined to prove a very acceptable substitute for higher-priced animal fats and does not propose, according to our understanding, to venture any ruling until the matter has had protracted scrutiny.

The editor of the National Provisioner comments on the foregoing as follows:

"It is evident that the government investigations have resulted favorably, since stearine made by this process is recognized and passed by the Bureau in meat inspection, the only requirement being that it shall be stated on the label that it is 'Stearine made from cottonseed oil' to indicate that it is manufactured stearine rather than the natural article." Editorial note in National Provisioner, Dec. 27, 1913.

Thompson notes that some criticism has been directed at the use of hardened oils for edible purposes on the ground that nickel is used in the process, but the manufacturers say that although nickel is generally used none of it is left in the oil, and that even if it were it is harmless, as shown by many tests with animals and with human "poison squads." Consular & Trade Reports, Dept. of Commerce, Jan. 14, 1914, 171.

* See also "Gehartete Pflanzenfette in der Speisefettindustrie," Der Seifenfabrikant, 1914, 181.

† Halbmonatsschr. f. d. Margarine-Ind., 1914, No. 4, 37; Seifen. Ztg., 1914, 206.

‡ Seifen. Ztg., 1913, 1317; J.S.C.I., 1914, 206.

§ Seifen. Ztg., 1913, 959.

been in use for ten years or more and during this period many people have eaten foodstuffs containing nickel, without any injurious effects being noted. Two publications have already discussed the matter to some extent, one being by Ludwig * and the other by Lehmann.† In one kilo of various foodstuffs these investigators found the following content of nickel:

Ludwig		Lehmann	
Spinach	25–27 mgs.	Beef and bouillon	26–64 mgs.
Peas	12–16 "	Potato pulp (equal part of water)	26–40
Lentils (acid)	35 "	Spinach	22.4
Lentils (boiled)	24 "	Damson plum mixture	13.3
Sourkraut	54–129 "	Sourkraut	18–57
Plums	35 "	Fruit cooked in 2 per cent acetic acid solution	65–67
		Water, salt water, flesh extract and milk	3.5–5.3

The whole question appeared of sufficient importance to lead Normann and Hugel to repeat this work. They used a nickel kettle to prepare the food material and ignited the product in a silica vessel to obtain the content of ash. Hydrochloric acid was then added to the ash and the nickel determined by Tschugaeff's reagent.‡ In this manner the nickel was determined gravimetrically in all cases, with the exception of coffee. In this latter case a colorimetric comparison with a nickel solution of known content was made.

Thus Normann and Hugel found:

	Duration of cooking, hours	Mgs. of nickel in one kilo of material
Coffee	½	0.03
Apple	½	46
Cabbage	¾	83
Red cabbage	1	67
Sourkraut	1½	127
Kohlrabi	1	19
Potato	¼	80

One of these investigators used a kettle of this character for a considerable period in his household. The food for the use of the family was cooked in the kettle so that food with a nickel content, approximating that of the above tabulation, was eaten, but no ill effects were observed.

* Osterr. Chem. Ztg., Vienna, Vol. I, No. 1, 1898.
† Arch. für Hygiene, Vol. 68 (1909), 421.
‡ Zeitsch. f. angew. Chem., 1907, 1844.

The determination of nickel in fats was made by igniting 200 grams of the fat in a silica vessel, dissolving the ash in hydrochloric acid, saturating the solution with ammonia, filtering to remove any precipitate of iron or alumina and evaporating the filtrate. To the residue was added 1 cc. of Tschugaeff's reagent (alcoholic solution of dimethylglyoxime) and ammonia (when a rose coloration due to nickel occurs). To determine the nickel quantitatively, the whole residue was dissolved in 100 cc. of water and the coloration compared with the color produced by adding the reagent to solutions of nickel chloride of known content. To secure a constant shade it was found desirable to allow the solution as well as the standard to stand for some time, usually over night, before final observations were made.

Of seven samples of hardened cottonseed oil examined, four samples contained 0.03 mg. of nickel in one kilo. One sample showed a relatively high content, 0.075 mg. of nickel; while the remaining samples contained 0.02 mg. of nickel. Palm kernel oil showed a content of nickel ranging from 0.017 to 0.1 mg. of nickel per kilo, averaging around 0.02 mg. Thus it will be noted that the nickel content of these fats is only about one-thousandth part of that found in foods prepared in nickel kettles, and when one considers that fats generally are not used for edible purposes, *by themselves,* but simply as additions to other foods, the amount of nickel furnished by hydrogenated fatty material amounts to so very little that the consumption of such food year in and year out may be regarded as harmless.

Even in fats intended for technical purposes, the amount of nickel is small as compared with that found in the food materials above mentioned, as for example:

	Nickel in one kilo
Hardened fish oil	3.3 mgs.
Hardened fish oil	1.2 mgs.
Hardened fish oil	3.2 mgs.
Hardened cottonseed oil	0.85 mgs.

Meyerheim* notes that oils which are to be hardened for edible purposes should be washed with alkali to remove fatty acid in order to reduce the tendency to solution of nickel by the oil; also that care should be taken in filter pressing to completely eliminate the particles of nickel catalyzer.

The propriety of using, for edible purposes, low-grade fats which have been deodorized and cleansed by hydrogenation has been made the subject of considerable debate. **Bohm** states † that when Mege

* Fortschr. Chem. Phys. and Phys. Chem., 1913, 305.
† Seifen. Ztg. (1912), 1087.

Mouries was working on the production of artificial butter it was far from his mind to use low-grade fats which had been purified by chemical treatment and that Boudet prescribed only fat of the best quality obtained from cattle slaughtered on the same day. Later when Huet claimed to make an edible product by thorough treatment of bad tallow with aluminium chloride solution, the margarine industry was hit a severe blow; for after such a proposal the opponents of artificial butter sought and with good results to prejudice the public against margarine.

Although to-day in a margarine establishment there is to be found the uttermost cleanliness as regards the plant, Bohm states that this is not true of the raw material before it comes into the hands of the margarine manufacturer. Even though, he declares, development of oil hardening may mean a great advance technically, it is coupled with such an opportunity for the employment of low-grade raw materials that it is likely to cause anxiety on the part of the public. In particular Bohm refers to the utilization of hardened fish oil in the margarine industry in which application technically it appears entirely suitable. Hardened fish oil, he states, is to be sure a chemically-changed, completely bacteria-free product; and physiologically is uninjurious. If, however, according to Bohm, we are to sanction the chemical treatment of fish oil, this would establish an important precedent for the application of all sorts of by-product fats and cadaver fats. When Hefter, together with other experts, formulated for the margarine industry the restriction that only those fats should be used which had been obtained from animals slaughtered under inspection, every consumer as well as every manufacturer of margarine was affected. With the inauguration of margarine manufacture from fish oil Bohm further states it appears not improbable that conflict with the present laws will arise.

Bohm refers to the assertion of Loock regarding *renovated* butter to the effect that no person who realizes the unpleasant properties of the original material would buy such butter, a statement, says Bohm, which can certainly apply equally well to whale oil margarine. Loock also cites a decision to the effect that no doubt exists that a food product is to be looked upon as unfitted for consumption when the raw material possesses a loathsome nature, irrespective as to whether the material through chemical treatment has been freed from such undesirable properties.

As to the loathsome nature of whale oil, Bohm asserts that one need only note the character of the methods employed in obtaining it in order to appreciate its undesirable nature. He maintains that a great part of the carcasses of whales are allowed to stand days at a time before they are worked up. Bohm indignantly declares the proposal to make an edible fat out of half-rotten whales which are treated in the hovels of the natives must naturally excite disgust. Perhaps, he says, a manufacturer of artificial butter may be able to use hardened fish oils in spite of the pure food laws, but may yet come into contact with the criminal courts, for when one buys margarine he expects to obtain freshly prepared beef fat and not a chemically-changed fish oil.

While this contention of Bohm may not be sound in some respects it is noted here for the sake of completeness. Naturally such an attack against a new and promising use for whale oil has not passed

unnoticed. See rejoinder by **Lieber** in Seifensieder Zeitung (1912), 1188, and editorial comment adverse to Bohm, also the opinion of **Keutgen.***

An oil which has been used so extensively by physicians all over the world as a remedial food for children **Lieber** believes cannot be looked upon as unsafe for human consumption. He calls attention to the hardy nature of the Eskimo whose principal or sole food is the blubber of the whale and seal. Furthermore, he contends that if the carcasses of whales were allowed to decompose, the oil which resulted would be of low grade and the pecuniary loss would be considerable. By the present system as soon as a whale is harpooned it is hoisted aboard the whaling ship and immediately rendered, the several grades of oil obtained being pumped to separate tanks. Every effort is made to produce the maximum yield of No. 0 and No. 1 oil because of the relatively high prices these bring.

Until seven years ago there was only a limited demand for whale oil, which was mainly used for the production of glycerine and fatty acids. It is now hydrogenated, for soap-making purposes, but in **Offerdahl's** opinion hardened whale oil is suitable for food. With regard to the traces of nickel present in the hardened oil, experiments showed that when small amounts of nickel powder were taken daily no ill effects were experienced, and that 99.8 per cent of the metal was rapidly excreted from the system. Hardened whale oils were found to be free from bacteria.†

The Halbmonatschrift f. d. Margarineindustrie (Dusseldorf) discusses the question of the prohibition of the use of whale oil in the edible fat industry (Seifen. Ztg. (1914), 30) and from this discussion the following is noted,‡ — Ever since the discovery was made of preparing an odorless and tasteless fat from whale oil by the hardening process it has been taken for granted in those circles which are antagonistic to the further development of the margarine and artificial edible fat industry that hardened fish, seal or whale oil could be used in the preparation of butter substitutes. This suspicion was all the greater because of the increase in the last few years in the cost of most of the raw materials used in the margarine industry. It has been customary for the agricultural opponents of butter substitutes to condemn the raw products from which these products are obtained and in this way to seek to make this indispensable article of food repulsive to the consumer. But in recent years the knowledge that margarine practically does not influence the price of natural butter, and therefore does not enter into competition with it, has gained some little headway. Dr. Vieth, Director of the Dairy Station in Hameln (an authority in his line) has acknowledged this to be a fact. If the margarine does not

* Seifen. Ztg. (1914), 89.

† Offerdahl, Ber. (1913), 558.

‡ See also the views of the Deutsche Margarine Zeitschrift (Seifen. Ztg. (1914), 118).

harm the butter industry, the bottom is taken out of the agitation which has been going on for over a decade against the manufacture of substitutes. In spite of this (Molkerei Zeitung, 1913) space has been lent anew to the suspicion that the raw materials used in the production of margarine cannot be entirely without effect.

Edible fats, such as hardened palm-kernel oil, cottonseed oil, etc., which have recently been introduced into the manufacture of margarine are thoroughly tested by government officials and scientific experts. The suspicion that infectious raw materials might be utilized can therefore apply only to the possible use of hardened whale and seal oil. In order, however, to prevent the spread of this idea and in order thereby to prevent a new danger to the butter substitute industry, the Duesseldorfer Margarine Zeitschrift suggests a legal prohibition of the use of whale oil in the edible fat industry.

It is supposed that the official foodstuff investigators will eventually aid this proposal. Its necessity is shown by the fact that an effort has been made from foreign countries to induce German margarine factories to use whale oil. The suggestion that well-known and reputable margarine factories have already started to use whale oil has been shown to be without foundation and is thought to be out of the question for the future. In order that no margarine made from whale oil may reach the German consumer because of unscrupulous manufacturers (and in that way the good name of a product which has been established only after many years of effort be brought into ill repute) but one remedy can be suggested: the prohibition of whale oil for food purposes. The trade journal of the margarine industry points out that such a value is placed by all classes of society upon margarine that the thought of utilizing any raw material repulsive to individual consumers ought to meet with vigorous opposition. It is evident from the editorial comment at the close of this article that the Seifensieder Zeitung is not in accord with the drastic views expressed in the foregoing.*

On the subject of hydrogenated edible oils but little has appeared in the literature.† A number of patents discuss various products and methods of preparation.

An edible oil composition is described by **Ellis** ‡ comprising hydrogenated cottonseed oil and cocoanut oil, the mixture being beaten with air to improve the color of the product. The following formula and method of treatment are given: Ninety parts cottonseed oil are mixed with ten parts of cocoanut oil and the mixture subjected to the action of hydrogen at a temperature of from 150° to 160° C., in the presence of finely-divided nickel so as to convert a large proportion of the unsaturated into saturated material. A solid composition is produced which is then subjected to aeration which may be carried out by beating the hydrogenated product with rapidly revolving

* Further comment by Keutgen on the same subject appears in Seifen. Ztg. (1914), 171.

† In an article on "Hydrogenated or Hardened Fat," appearing in the National Provisioner, Sept. 27, 1913, 104, Hall observes that hydrogenation is one of the greatest advances ever made in the fat and oil field.

‡ U. S. Patent 1,037,881, Sept. 10, 1912.

paddles until a sufficient quantity of air is incorporated in the product, in a finely-vesiculated condition to produce a material of the proper consistency and light colored appearance. Another statement * gives details of a hydrogenated butter substitute in which various hydrogenated and normal oils are incorporated to make a fat approximating the melting point of butter, with which is mixed milk, etc., to produce a variety of margarine. These compositions should ordinarily have a melting point considerably less than the temperature of the human body, so that when the material is taken into the mouth, it immediately melts and does not leave a greasy sensation on the tongue and walls of the mouth. It is generally desirable to carry the hydrogenation treatment to a point where a product of rather firm consistency is secured. This produces a material, however, which is of too high a melting point for the production of a vegetable butter composition. Hence it is then pressed to remove the excessive amount of stearin. In the case of cottonseed oil, it is stated that it is desirable to hydrogenate until the iodine number falls to about 80. The oil may then be cooled to about 30° C., and allowed to stand for a time and pressed. Afterwards it is warmed to render it entirely fluid, and is incorporated with milk material. Suitable material of this character is ordinary full milk or skim milk or butter-milk, sterilized milk, sour milk or milk which has been specially fermented. Coloring material, such as ordinary butter color, may be added. Also a flavoring compound, such as cumarin and various esters and aldehydes, such as those of valerian and capryl bodies, may be added. In order to give the product the property of browning, when heated in a skillet, bodies such as egg yolk, milk sugar, lecithin or finely-powdered casein may be introduced.

A suitable oil base having been derived in this manner, the oily material is emulsified with the milk material to thoroughly mix the latter with the fatty body. For 100 parts of fatty material about 30 to 60 parts of full milk or perhaps 50 to 80 parts of skim milk are suitable proportions. In the summer months a stiffer composition is required than in the winter months and the fatty material should be compounded to give a material melting at the proper point with reference to seasonal temperatures. In emulsifying it is desirable to put a portion of the milk in the beating apparatus, and to stir for a short time. In the case of full milk, beating for 10 minutes or so causes a separation of the butter fat. The oil may then be added in portions, beating thoroughly until the composition is well incorporated. The remainder of the milk and fatty material may be added

* Ellis, U. S. Patent 1,038,545, Sept. 17, 1912.

from time to time, and the temperature of the mixture should preferably be maintained between 30° and 40° C. When the composition has become thoroughly incorporated, it is run from the apparatus into a cooling device which cools the emulsified composition rapidly. It is then ready to be rolled and kneaded to remove the excess of water, etc., after which treatment the material is formed into the desired shape for shipment. The coloring material and salt and also flavoring material may be added during the emulsification process if desired.

The use of hardened oil in preparing oleomargarine compositions is the basis of French Patent 458,611, of 1913, to **Deveaux.**

Hydrogenated soya bean oil * has been recommended, as well as hydrogenated vegetable oil and animal fats mixed to form lard-like products of varying composition. When employing cocoanut oil in such compositions it is desirable to hydrogenate it. To be sure, cocoanut oil usually has an iodine value of only 7 to 10, which is indicative of the small proportion of unsaturated bodies present. But, in spite of this, in order to secure a permanent product, which does not separate or grow lumpy on standing, and which remains in a perfectly neutral condition for a long period of time, even when exposed to the air, it is desirable that the iodine number of the cocoanut oil should be reduced to practically zero, if larger proportions than 30 per cent or thereabout are incorporated with hydrogenated soya bean or cottonseed oil.

An edible product of a superhydrogenated character † is obtained by carrying the degree of hydrogenation beyond the actual titer required and then pressing to remove some of the harder material so that the final titer of the expressed fat is that of lard, butter or whatever other titer may be required. Most oils of a vegetable nature and some animal oils contain from traces up to considerable quantities of highly-unsaturated bodies, including those of the linoleic and linolenic group. These and other similar bodies are very sensitive to oxidation and lend instability to edible oil products of this character by their tendency to change chemically and thus alter the flavor of the material. These bodies may be saturated by very careful hydrogenation up to the degree of consistency required in the edible product, but such hydrogenation is difficult to carry out commercially on a large scale with the assurance that the product will run uniform in quality. By saturating these bodies with hydrogen to an excessive degree as regards final consistency, these bodies lose their identity and become substantially free of odor of origin and tendency to rancid-

* Ellis, U. S. Patent 1,047,013, Dec. 10, 1912.
† Ellis, U. S. Patent 1,058,738, April 15, 1913.

ify or otherwise be decomposed. By hydrogenating cottonseed or corn oil or similar oils to materially reduce the iodine number, the more sensitive double bonds are saturated with hydrogen and thereby eliminated and oxidation tendency is reduced to a minimum. Apparently the complete elimination of all the double bonds characteristic of the linoleic type is more difficult than the removal of the double bonds characteristic of the linolenic type, so that control over this seeming selective action during hydrogenation when saturating up to a given degree of consistency from a given oil is difficult, if not impossible, under ordinary conditions of hydrogenating. If, however, the oil is overhydrogenated so that a more consistent fat is acquired than is actually desired for an edible product, the unstable bodies thus may be completely transformed. In order to secure the degree of consistency desired the hot hydrogenated fat is gradually cooled to about 30° C., when the temperature may be maintained between 25° to 35° C., or so for several hours to induce crystallization or balling of the high melting point compounds. The mass is then pressed to the desired degree. Such a superhydrogenated pressed product which may be made either of butter-like or of lard-like consistency is stable in storage and is not liable to coagulate on standing with the formation of objectionable masses of granulous stearin-like bodies.

It has been noted when a vegetable oil such as cottonseed oil is hydrogenated directly until of the consistency desired that on cooling frequently it tends to granulate unless chilled or very rapidly cooled. This is objectionable in culinary operations as an initial lard-like body after once heating and slow cooling in the air often forms relatively hard granules of stearin-like bodies which look like little balls of coagulated material and separating as they do from the fluid oil under some circumstances give the product the appearance of having curdled or decomposed. By super-hydrogenating and pressing to the point required the granulating stearins or stearin-like bodies are eliminated to a greater or less extent and less easily crystallizing or non-granulating stiffening bodies remain tending from their amorphous texture to better maintain the original consistency and appearance of the product in repeated culinary use.

The **Boyce** process * of producing an edible compound consists in preparing a mixture of synthetic stearin by the action of hydrogen in the presence of a catalyzer upon a previously unsaturated oil or fat, the latter being subjected to the catalytic action of hydrogen to a

* Boyce, U. S. Patent 1,061,254, May, 6, 1913, assigned to the American Cotton Oil Co.

degree sufficient to convert the required fraction of the oil into synthetic stearin. The hydrogenation process is arrested at the point when the stearin is found to be present in the amount of about 20 per cent of the entire body of the oil. Boyce states that by arresting the action at this point there will remain a mixture of the unsaturated oil and the synthetic stearin produced by the hydrogenation of a portion of the oil.

A hydrogenated fatty food product containing hydrogenated corn oil has been described.* When corn oil is suitably hydrogenated, a product is derived which has the property of improving the stability of hydrogenated cottonseed oil or similar hydrogenated oils which tend to granulate. Also it is stated that hydrogenated cocoanut oil may be used as a fluxing agent for chocolate in the manufacture of confectionery. The melting point of the fatty flux should preferably be about 90° to 100° F. Hydrogenated cocoanut oil olein may be used in a similar manner. The manufacture of the coating of chocolate creams calls for a relatively high melting point fat which incorporates readily with chocolate and does not impair its flavor. Cocoa butter is especially desired on this account, but is relatively expensive. Cocoanut oil melts so easily that in hot weather candies made with it soften very quickly when handled. Cocoanut oil also has a tendency to rancidify. By hydrogenation of an oil assimilable with chocolate the exact melting point desired may be obtained and a stable composition secured.

Hydrogenated oil of high titer, as stated, may be mixed with unhydrogenated oil to form a body of a consistency suitable for use as a substitute for lard. For example, hydrogenated cotton oil of a titer of say 52° C. (fatty acids) may be melted and incorporated with four times its weight or so of ordinary refined or deodorized cottonseed oil so as to form on cooling a white, opaque fatty material of the consistency of ordinary lard. The product made in this manner is not always sufficiently stable. Not infrequently in a short time it will lose its opacity to a considerable degree and will take on an appearance more suggestive of petrolatum than lard. Sometimes this change, which may be due to a tendency to form solid solutions of certain types, occurs irregularly in layers or isolated zones which give the product a curious mottled appearance, and this striated effect taking, place in the containers during storage so changes the product, physically at least, that it is regarded as damaged or unfit for use by those accustomed to the normal appearance of lard. By disseminating through a fatty basis of a melting point and consistency approaching that of

* Ellis, U. S. Patent 1,067,978, July 22, 1913.

lard, a quantity of fatty material of higher titer so as to form flocculations of a high titer product uniformly disseminated through the fatty basis, a product of better " color stability " is secured.* The material of the relatively higher titer may be denominated the stabilizer and the proportions of fatty basis and stabilizer as well as their melting points and titers may be varied to meet various conditions of a climatic nature.

As an illustration one may take to make the fatty basis, 6 parts of hydrogenated cottonseed oil of a titer ranging between 52° to 54° C. (fatty acids) and 34 parts of refined and deodorized cottonseed oil. A thorough mixture is secured by the aid of heat and when well incorporated the melted product is chilled rapidly in a thin layer by feeding onto a chilled roll which is kept in constant rotation and from which the solidified product is removed in layers by a scraper. This product when properly set has a consistency approaching that of ordinary lard. The stabilizer is prepared by incorporating 3 parts of hydrogenated cottonseed oil of the same titer as that used in making the fatty basis, with 5 parts of refined and deodorized cottonseed oil. By heating the hardened oil with the deodorized oil the requisite mixture is obtained. As in making the fatty basis, the stabilizer is likewise chilled to form a solid, preferably in thin layers, and the two products are mixed in powerful mixing apparatus until the stabilizer is well disseminated through the fatty basis. To secure a desirable distribution both the fatty basis and the stabilizer may be fed onto the same chill roll in a series of adjacent or alternate streams, or the fatty basis may be allowed to fall on the chill roll, and when it has progressed a distance sufficient to solidify but not to stiffen it fully, the stabilizer is applied as a superposed coating adherent to and slightly intermingled at the contacting surfaces, with the fatty basis. This composite film is removed by the scraper and is then "pugged" or beaten. As the melting point of the stabilizer is preferably considerably higher than that of the fatty basis, the former congeals more quickly, so that although the superposed film is somewhat insulated from the chill roll by the fatty basis film yet the solidification of the upper layer is usually rapid enough to prevent material solution or interfusion of the two heterogeneous layers.

Further modifications are the following: Eighty parts of cottonseed oil are mixed with fifteen parts of hydrogenated oil of a titer of 48 (fatty acids). This is chilled and mixed with five parts of melted 42° C. titer hydrogenated or hard oil, or fat. Likewise one can superpose on a basis of 34 to 38 titer about 20 per cent of 40 to 42 titer. Cottonseed oil may be hydrogenated to 37 titer, chilled as described and similarly incorporated with about 10 to 20 per cent cottonseed oil hydrogenated to 40 to 42 titer. Thus there may be obtained a lard-like or otherwise consistent fatty material having its main titer to a considerable degree influenced so that the product may have the desired soft consistency of ordinary lard while actually containing bodies which if melted into the fatty basis would raise the melting point and consistency.

Palm oil, suitably hydrogenated, has been recommended for use in edible fat products. †

* Ellis, U. S. Patent 1,070,331, Aug. 12, 1913.

† Ellis, U. S. Patent 1,087,161, Feb. 17, 1914.

The fatty acids of Kaya oil have been hydrogenated by Ueno (Chem. Rev. u. d. Fett. u. Harz. Ind. (1913), 209) who thereby obtained fatty acids melting at

Wilbuschewitsch * regards his process as applicable to the treatment of all unsaturated acids and their glycerides, as well as for waxes and other alcoholic fatty substances. From castor oil there is obtained a product which melts at 83° C. The finished fat can be hydrolyzed and the fatty acids distilled. For example, from cottonseed oil there may be obtained fatty acids which melt up to 71° C. and make excellent candles. After suitable refining the products may yield satisfactory alimentary fats if the reduction is only carried so far that the melting point is between 28° and 34° C. Thus he finds from castor oil there may be made a product which is odorless and tasteless but retains the other properties of castor oil. So also from cod liver oil and other fish oils there may be made butter substitutes, or from vegetable oils substitutes for cocoa butter. Oils treated by the process lose their specific odor.†

65.5° C. The hydrogenation of the material was carried out in alcohol solution using platinum black as a catalyzer. Kaya oil as employed for edible purposes is liquid and yellow in color.

* U. S. Patent 1,024,758, April 30, 1912.

† The keeping properties of some hardened oils examined by Knapp (Analyst, 1913, 102) were found to be remarkably good. Although prepared nearly a year and a half previously, and having often been exposed to damp air, yet these samples showed no signs of rancidity. The acidity (0.7 per cent as oleic acid) did not appreciably change during the period of observation.

CHAPTER X

USES OF HYDROGENATED OILS AND THEIR UTILIZATION IN SOAP MAKING

Uses of Hydrogenated Oils

Liquid fats and fatty acids are essentially cheaper than solid fats and fatty acids, and the ability to prepare from ordinary *liquid* fatty oils a fatty body of almost any desired degree of consistency or hardness renders hydrogenation especially attractive in the production of edible fats and soap-making materials. These are, undoubtedly, two of the most important applications, although hydrogenated oils are likely to have a rather wide use in the arts. In the manufacture of insulating compositions and lubricants, for example, the hydrogenated fats may be used to advantage. In the tanning industry the stearin produced by hydrogenation is being used as a substitute for oleo-stearin.

The physical and chemical properties * of hardened oils, particularly the hardened fish oils, indicate that these products are useful in the manufacture of lubricants and that they may be used as a substitute for tallow in the preparation of various lubricating compounds.† In compounding preparations of this character, the requisite amount of hardened oil is added to the oil base employed, the mixture being heated to secure satisfactory incorporation, and then is cooled, when it is ready for use. The better grades of hardened fish oil also can be used alone as a substitute for acid-free machine tallow.

A review of the soap trade of the United Kingdom for 1913 is significant in indicating decreased requirements of several of the staple raw materials, which condition, rather than suggestive of any decline in the production of soap, marks a greater dependence upon supplies which have been brought within practical operation largely through the hydrogenating process for hardening oils. To quote from the report on this subject:

"It is of the greatest moment that the European soap maker has found in the hardened oils produced by the hydrogen process very considerable relief from factors that must have driven values very much higher, had not this new source of supply come into actual operation."

* Seifen. Ztg. (1912), 1092.

† Hydrogenated fats, Leimdorfer states (Seifen. Ztg. (1913), 1317), can be used in the preparation of lubricants and in tanning operations.

"English manufacturers as a rule are quick to turn to advantage any opportunity to exploit new methods and processes in their industries, and the recognition of the practical application of hydrogenated oils in such an important field as soap making is a development of much interest to the affected trades in this country, where the process in its general relationship to the soap and lard compound industries is in a more or less experimental stage. According to the English soap trade report the losses in three of the leading materials available for home consumption, as measured by the excess of imports over exports in 1913, were 3532 tons of tallow, 1656 tons of palm oil and 2240 tons of cocoanut oil. Exports of soap from the United Kingdom last year were heavier (1732 tons), while imports from foreign countries were lighter by 2194 tons. As a result of the strides in the hardening of materials for soap production by hydrogenation, whale and linseed oils are now accorded an established place in the Kingdom's soap industry. The total capacity of the hardening plants in Europe, including the United Kingdom, is given as 220,000 tons of oil, although some of the views expressed in the local trade place it to 300,000 tons. A good part of the American linseed oil export trade last year has been attributed to the heavier requirements for the soap kettle through the hydrogenation process, and crushers and dealers have been buoyed to keener expectations for this year's foreign business. Conditions in other fields in which linseed oil enters must, however, be reckoned upon as contributing factors. Persistent attempts have been made to induce our soap makers to adapt hardened linseed oil to their service, and while sales of round parcels have been made for this account, so far as is known none of the purchasers has been encouraged to put the oil into actual test. The favorable market conditions for competing fats in the soap field may have accounted for the attitude of makers toward linseed oil for this particular purpose."

"Probably the greatest headway in the application of the hydrogenating hardening process in this country has been in the field of edible products in which cottonseed oil has entered on the most liberal scale. It was through this means that the domestic consumption of refined oil during the last crop year so surpassed the general expectations of the trade that the principal markets abroad were scoured last summer to reclaim any supplies of our oil that might be available, and foreign producing sources were also called upon to help relieve the stringency here."*

Auerbach† considers the hydrogenation process responsible for an advance in the price of fish oils so that they will be of doubtful benefit to the soap industry. Also he states that the so-called burned odor which was noticeable in soap made from hardened fats is said to have been overcome. Besides fish and whale oil, he notes that castor oil is treated to some extent. The hardened castor oil is used for insulation purposes in the electrical field.

Hydrogenated Oils in the Soap Industry

The developments in oil hydrogenation have brought to the soap industry an innovation of fundamental importance in the domain of raw materials. The soap manufacturer, no longer well able to purchase the best grade of fats in face of the high prices paid by the margarine and other edible fat industries, has now at his disposal the

* Oil, Paint and Drug Rep., Feb. 2, 1914.
† Chem. Ztg., **37**, 297.

means for utilizing lower grade materials in substitution for more costly stock.

By hydrogenation, oils which formerly made soaps only of soft consistency, now yield the more valuable hard soaps. This has led to a very rapid development of the art with respect to the production of soap-making fats. In particular, fish and whale oils have been made use of, because these oils may be completely deodorized by the addition of hydrogen.

According to a Japanese chemist, **Tsujimoto,** the odor of fish oil is due almost entirely to a fatty constituent and not to so-called impurities. This fatty constituent is clupanodonic acid having the formula $C_{18}H_{28}O_2$, which, therefore, by the addition of 8 hydrogen atoms, becomes stearic acid. When hydrogenated down to an iodine number of about 50, fish oil has the consistency of hard tallow and the odor of fish oil is wholly absent. Even the fishy taste is scarcely in evidence.

For soap making this product is satisfactory as it complies with the test for a deodorized fish oil suitable for soap making in that the odor of the original oil is not apparent when ironing laundered goods on which such soaps are used. If, however, at least with the poorer grades of oil, the hydrogenation is not carried on to a point where the iodine number is approximately 50 or less, there is some danger that the fishy odor will become apparent during the ironing operation.

It appears not improbable that unstable odor-forming nitrogenous impurities in fish oil add hydrogen during the hardening process and are transformed into bodies of a stable character.

Data on a hydrogenating plant in Norway is furnished by Commercial Agent E. W. Thompson of the Department of Commerce (Consular & Trade Reports, Jan. 14, 1914, 171) who reports that during the summer of 1913 an oil-hardening plant was opened at Fredrikstad by De Nordiske Fabriker, with head office at Christiania.* The original object was to harden whale oil for the soap industry, but as the result of experiments with edible oils the plant is being enlarged to a capacity of 1000 barrels a day with the expectation of hardening cottonseed and peanut oils for the margarine makers. If this plan is successful it may double the

* This concern is said to be a German-Norwegian company, capitalized at about $833,500, organized to work a new German method of hydrogenation. The Hafslund Falls are being utilized to generate the electric power required by the work and also to manufacture by electrolysis the hydrogen required for the hardening process to which the purified whale oil is submitted and converted into a solid neutral fat. The daily consumption of oil is about 300 barrels. (Jour. Ind. and Eng. Chem. (1913), 608.) The hardened fat has a melting point between 40° to 50° C. and is stated to be odorless and tasteless. Although at the present time principally used for soap making, in all probability in due course the material will be employed in the manufacture of edible fats. (Seifen. Ztg. (1913), 1413.)

consumption of cottonseed oil in the margarine industry. The Norwegian firm will purchase the best grades of cottonseed and peanut oils, and will also harden on toll. Many European margarine factories are experimenting on hardened cotton and peanut oils to replace copra oil, which is high in price.*

Some criticism has been directed at the use of hardened oils at least for edible purposes on the ground that nickel is used in the process, but the manufacturers say that although nickel is generally used none of it is left in the oil, and that even if it were it is harmless, as shown by many tests with animals and with human "poison squads."

Samples of Norwegian hydrogenated whale oil which have come to the author's attention are of exceptionally high quality.

Whale oil of the grades known as 0 and 1 hydrogenate readily with nickel as a catalyzer. No. 2 is somewhat more difficult and No. 3 is decidedly troublesome to treat without special refining.

Chinese wood or tung oil may be rendered very hard by thorough hydrogenation and the product often shows the property of expanding on solidifying from a melted state, forming a friable mass instead of a firm block. Hardened linseed oil sometimes exhibits a like behavior.

Hardened chrysalis oil is described by Tsujimoto (Jour. Chem. Ind. Tokio, 1914, No. 191 and Chem. Ztg. Rep. 1914, 110). Hydrogenation was carried out with a nickel catalyzer and traces of nickel were found in the ash of the hardened product.

Soya bean oil has become an important raw material for hydrogenation purposes. (Seifen. Ztg., 1914, 348.)

The commercial side of fat hardening is discussed to some extent by Schicht † and the value of fish and whale oils in this field is considered. The probable place hardened fats will assume in the soap and edible fat industry is discussed in Seifensieder Zeitung (1913, 768).

In this country very little has as yet appeared in the literature regarding the application of hydrogenated oils in soap making, but in Germany considerable space has been given by the trade journals to discussions of the subject. Some of the statements are of a very contradictory character as is, of course, to be expected in the early stages of development of this important subject, especially in view of the very considerable degree of empiricism which prevails in some branches of the soap-making industry.

It is to be regretted that so much of the published matter relates to products offered under trade names such as Talgol, Candelite and

* Hardened sunflower oil is mentioned in Seifensieder Zeitung (1913), 611. The Knowles Oxygen Company, of Wolverhampton, England, has contracted with the Sunlight Soap Factory, in Port Arthur, to erect an annex to the plant for the production of the hydrogen necessary for hardening palm oil; the oxygen is to be collected and sold.

† Seifen. Ztg. (1913), 287.

similar hydrogenated fish and whale oils, etc., of the Germania Oelwerke at Emmerich, but while soap making as practiced in Germany differs in several respects from the practice in this country, it is believed the work abroad will prove at least suggestive if not instructive.*

In the following an attempt has been made to briefly review the more important contributions in this connection.

Garth † states that fish and whale oils are the raw materials for a considerable proportion of the hydrogenated products which, up to the present time, have found application in soap making. Being relatively low-priced raw material many attempts have been made to make cheap soaps from fish oil. These attempts in the past have been unproductive because the objectionable odor reappears after goods are laundered. Hence there are many proposals directed toward the production of odorless fish oil. As is known fish oil contains nitrogenous compounds and certain of the lower fatty acids arising from decomposition of the fish before the oil is expressed. Most of the proposals are based upon the assumption that these sources of the evil odor can be removed by the action of energetically-reacting bodies such as sulfuric acid and the like. However, neither treatment with strong acids nor distillation with superheated steam produce unobjectionable products. By hydrogenation the disagreeable odor disappears; nevertheless, there always remains an odor similar to that of distilled olein which, however, is completely concealed if the product is worked up with a goodly proportion of other fats.

Garth ‡ observes that the hydrogenated fats which have been used in the soap manufacture appear in the trade as Talgol, Talgol extra, Candelite, Candelite extra, Crutolein, Talgin, etc. Talgol has a melting point of 35° to 37° C., and an iodine number of 65 to 70. Talgol extra melts at 42° to 44° C. and the iodine number is 45 to 55. The Candelite products are harder, Candelite melting at

* In England one large concern is offering several grades of hardened fat ranging as follows:

	Iodine No.	M. P.	Titer
A1	50	40–42	36
A2	85	28–30	32
C1	60	44–46	45
C2	75	35–37	36

† Seifen. Ztg. (1912), 1278.

‡ Seifen. Ztg. (1912), 1279.

48° to 50° C., and having an iodine number of 15 to 20, while Candelite extra melts at 50° to 52° C. and exhibits an iodine number of 5 to 10.*

Heller † furnishes the following data on these products:

	Acid No.	Saponification No.	Unsaponifiable	Iodine No.
Talgol	3.5	190.7	0.33	63.9
Talgol extra	3.8	190.5	0.31	36.1
Candelite	3.8	190.4	0.41	18.4
Candelite extra	4.4	188.4	0.52	10.4

FATTY ACIDS

	Melting point	Titer	Acid No.
Talgol	38.5	34.6	199.7
Talgol extra	45.5	43.5	199.9
Candelite	48.5	47.4	198.9
Candelite extra	51.8	50.5	199.9

Schaal has reported ‡ the results of his observations on the two products Talgol and Candelite derived by hydrogenation of fish oil, etc., and has called attention to the adaptability of these hardened fats in the production of soap base or milled soap. Both Talgol and Candelite have a tallowy appearance with this difference, that one is softer and one is harder than tallow. At first glance one is likely to regard these fats as similar to high-grade soap tallow, but the odor of the product immediately shows this is not the case. The odor is not disagreeable and in fact resembles some grades of tallow. It is suggestive of the cheesy odor given off by tallow which has been stored for a considerable time in warm weather. Of the two products Talgol and Candelite, the odor in the latter is less noticeable.

In his first investigations Schaal simply replaced a part of the softer fats, as he thought Talgol would lose its firm consistency during the

* The Ölwerke Germania has trademarked in the German Patent Office the words Andelite, Candolit, Cancellit, Coryphol, Doratol, Dural, Durettol, Durolit, Durotin, Durotal, Duru, Durutol, Jutol, Jutolin, Kandel, Kandelin, Kandetil, Kandorit, Kerzenit, Kritolit, Krunotin, Krutello, Krutol, Krutolin, Talgela, Talgelin, Talgol and Urutol. (Taschenkalender f. d. Oel und Fett Industrie, 1914.)

† Seifenfabrikant (1912), No. 31.

‡ The results of investigations by Schaal on the utilization of hardened oils in soap manufacture are published in the Seifensieder Zeitung (1912), 821, 846, 954 and 979; (1913), 173, and in a book entitled Die Moderne Toiletteseifen-Fabrikation, Augsburg, 1913, to which reference should be had for detailed description.

boiling operation and would return to a consistency approaching that of the original oil. This assumption proved to be unwarranted as tests with small samples showed that the Talgol fatty acids were as hard as the Talgol itself. The first fat mixture used for preparing a soap consisted of the following:

40 parts tallow.
15 parts Talgol.
30 parts bone fat.
15 parts cocoanut oil.

No rosin was used as it was desired to determine the influence of the Talgol odor. During the boiling the odor of Talgol was plainly in evidence, much more noticeable in fact than could be observed afterwards in the finished soap. The dried curd exhibited a wholly agreeable odor in which the characteristic odor of Talgol could not be detected, and no odor was in evidence of a nature calculated to affect the perfume. The soap was not perfumed, but was wrapped in paper and laid aside a few weeks for further observation. In another trial the tallow was reduced and the Talgol increased in amount, the formula being:

25 parts tallow.
35 parts Talgol.
30 parts bone fat.
10 parts cocoanut oil.

The saponification progressed satisfactorily, indicating that Talgol readily united with alkali. As the bone fat employed was of exceptionally dark color, the soap was bleached in the kettle with 0.2 per cent Blankit. The dried product had a fine ivory white appearance, but the odor of Talgol was apparent although not so pronounced as to render the soap unusable. This soap base milled very smoothly and easily, giving an excellent finish. In another trial 5 per cent of rosin was introduced with improvement in the odor of the soap base.

The milled and perfumed soap was kept under observation and it was noted that some perfumes were affected by the Talgol odor. A person with a keen sense of smell would immediately detect the presence of Talgol. Tests were conducted with a number of perfumes* including hyacinth, lilac, rose, pathouly and violet, each cake being separately wrapped in parchment paper. It was found that the two first-mentioned perfumes were more sensitive to the presence of Talgol smell and gave a momentary impression that the soap had become

* Schaal gives a number of perfume formulæ for hydrogenated oil soaps in Seifen. Ztg. (1912), 979.

rancid; the rose was slightly affected while the other samples were not noticeably changed. Schaal reaches the conclusion that the highest grade of toilet soap perfumed with delicate essential oils is affected by the use of Talgol or Candelite and that these hardened oils will not find an application here. Such soaps are, however, sold only to very fastidious trade and require in any case perfumes of the very highest grade. On the other hand, in manufacturing ordinary grades of toilet soap which are, of course, made in enormous quantities, up to about 35 per cent of Talgol or Candelite may be employed advantageously in the fat stock. As regards solubility in water and free lathering properties, Schaal found Talgol or Candelite to afford satisfactory results, the soaps which he prepared forming a lather immediately which was thick and voluminous, acting in fact like any standard soap. It is reported that the Ölwerke Germania has been successful in producing a completely odorless product at a somewhat higher cost. If such a deodorized product can be put out at reasonable price, it will be possible to make toilet soaps of the highest grade with hardened fats derived from relatively cheap oils.

Of Talgol, Schaal notes that the fat is readily deprived of its glycerine and especially well by the Krebitz process,* and soaps made from this stock are prime products.

Schaal states that so long as these hardened fats are not entirely odorless, as indicated they cannot be advanced for the manufacture of soap stock of the first class. For these, the best beef tallow, etc., must remain the raw material, for this class demands the best that the soap industry can produce. Talgol is therefore considered suitable only for working up into soap stock of second and third grade. In these soaps the price of raw material plays a considerable rôle, and thus Talgol proves an advantageous substitute for tallow. Pure Talgol soap has too little lathering power and as its odor is also objectionable it is not advisable to allow the addition of Talgol to rise above 40 per cent. The lathering power will be considerably better if 10 per cent of palm kernel or cocoanut oil is worked in and the solubility of the soap is also much increased. If, however, 60 per cent of other fats are present, bad lathering is prevented, and the product meets the requirements of the trade. The yield of pure salted soap on the average is 165 per cent.

The following are some recipes given by Schaal for soap stock of two grades.

* The Krebitz process is recommended for the treatment of hardened fats in the manufacture of toilet soaps. (Seifen. Ztg., 1914, 391.)

Soap Stock, Second Grade

(1) 30 parts Talgol extra;
40 parts beef tallow;
15 parts peanut or corn oil;
15 parts cocoanut oil.

(2) 40 parts Talgol extra;
25 parts beef tallow;
20 parts peanut or corn oil;
15 parts cocoanut oil.

Soap Stock, Third Grade

(1) 40 parts Talgol extra;
15 parts beef tallow;
30 parts oleomargarine waste, bone fat, hide fat, etc.;
10 parts palm kernel oil or cocoanut oil;
5 parts rosin.

(2) 40 parts Talgol extra;
30 parts oleomargarine waste, bone fat, hide fat, etc.;
20 parts bleached palm oil;
6 parts cocoanut oil;
4 parts rosin.

It may be noted that with each increase in the amount of Talgol, a similar increase in the amount of softer fats is demanded. Talgol extra is a rather hard fat and easily permits a considerable addition of fluid fats, producing a pliable plastic soap base which can be easily milled. Talgol like tallow is saponifiable with some difficulty and for the complete combination of it with alkali, boiling for a number of hours is required. The boil must be conducted with weak lyes of 15 to 20 degrees in order to get a good combination of fat and lye. With respect to the odor of the soap it is an advantage if the reaction between the fat and lye is extended over as long a period as possible, since the odor of Talgol thus almost completely disappears. When possible the Talgol material should be well blown with steam in the kettles, as by this treatment the odor is almost completely removed.

The resulting soap base displays absolutely no difference from that of a straight tallow stock, and works up on the machines exactly as a soap from beef tallow; indeed it may be said that milled soap from Talgol has a finer, cleaner and whiter look than that made without it. The odor may be permanently concealed in finishing the soap by means of appropriate perfumes.

The tests made by Schaal of Talgol as a constituent of cold process soaps led to the conclusion that it only has value in combination with cocoanut oil. The saponification of Talgol may be accomplished with strong tepid lyes if the following conditions are observed. First the temperature of the fat at the moment of contact with the lye must be at least 50° C. and on cold days about 55° C. It is desirable to warm the lye to 25° to 30° C. before incorporating. It often happens on mixing that the whole mass suddenly solidifies so that the mixture must be warmed to liquefy. Even when the temperature of the bath is higher than the figures given, solidification takes place

on running in the cold lye, or at least small lumps are formed. The union of the fat and lye takes place very quickly; the mass becomes solid in a short time and can be framed. On this account the frames must be ready at hand. In the frames a rather strong reaction sets in, and heat is generated. The frames should be well covered to take advantage of this rise in temperature. The finished soap is very hard and almost brittle in character and on this account must be cut while fresh. It has a fine white color, but is not transparent. The odor is not unpleasant, and varies with the fat used; it can be completely covered by oil of citronella or lavender. Artificial oil of bitter almonds is less adapted to permanently cover the Talgol odor.

The following is a useful formula:

25 parts Talgol,
25 parts Ceylon cocoanut oil,
5 parts castor oil,
28 parts caustic soda lye, 37° Be.

The mixture of fats at a temperature of 45° to 50° C. is stirred well with the lye, which need not be warmed. In about one-half hour reaction is under way and the product should at once be framed. If delayed longer, the mass becomes almost in a moment solid and must be warmed to soften. This is unnecessary if the frames are ready at hand as above cautioned. This soap heats up strongly in the frames and on cooling is plastic with a somewhat transparent look. It lathers freely like a shaving soap and when properly perfumed is an excellent product. Such a soap is well adapted for pressing, which gives it a fine solid appearance.

For cocoanut oil soaps which are to be filled, 25 per cent of Talgol is recommended. Such soaps cut and press well and have a good solid feel. The batch should be maintained at a temperature of 40° C. when stirring, lest the soap get too solid before the filling is worked in. If this temperature is maintained no trouble need be feared with the lye or the filling. In weighing off the oil it is to be noted that the cocoanut oil should be first introduced and then the Talgol. Otherwise the latter sticks to the side of the kettle and the entire mixture then has to be made hotter than is necessary. 75 per cent of filling can be incorporated with 25 per cent of Talgol, giving a yield of 225 per cent without danger that the filling will settle out or fail to be held up. The soap is moulded as soon as thick and the moulds left covered for two hours. The cooled soap is hard and tenacious but still may be readily pressed. For filling, any desired solution of salt, potash and sugar in water may be employed.

The following is an appropriate recipe for a soap of this class:

22½ kilos Ceylon cocoanut oil,
7½ kilos Talgol,
16½ kilos caustic soda lye, 37° Be.,
22½ kilos filling solution,

perfumed with 200 grams of oil of citronella or 200 grams of lavender or 100 grams of each oil.

For soaps with more than 75 per cent filling and yields of 250 per cent and over it is best to conduct the process in the warm way.

A cold process shaving soap made from 80 per cent Talgol extra and 20 per cent cocoanut oil exhibited satisfactory lathering properties, but in spite of strong perfuming the Talgol odor eventually reappeared, especially at the surface of the cakes.*

In a discussion of available substitutes for palm kernel oil † it is stated that hardened fish or whale oil such as Talgol cannot be used as a substitute for palm kernel oil. The peculiar musty odor of Talgol, which to be sure no longer resembles that of the original oil, is, however, decidedly penetrating. Several grades of soap made with Talgol and Crutolein yielded a soap of too pronounced an odor to be marketable. Soap containing these hardened products was made into a soap powder and although the percentage of the hardened fat in this product was low, its presence was still detectable by the odor. It is, however, stated that if means can be found for the removal of this characteristic odor, the situation as regards the general utility of these hardened fats will be entirely altered.‡

* Weber, Seifen. Ztg. (1913), 421.

† Seifen. Ztg. (1913), 312.

‡ Neither tallow, palm kernel or cocoanut oil can be completely substituted in soap making by hardened fish or whale oil, but the latter may be used to advantage as an addition fat in laundry soaps. (Seifenfabrikant (1913), 30; Zeitsch. f. ang. Chem. (1913), 310.)

Leimdorfer (Seifen. Ztg. (1913), 284 and 310) treats of hardened fats with special reference to the soap industry.

The addition of hardened oil to other soap stocks is advantageous for lowering costs and gives a satisfactory product when not used to excess. When caustic potash is used for saponifying a mixture of 65 per cent cottonseed oil and 35 per cent Candelite the soap does not grain but remains clear. (Seifenfabr., **33**, 30.)

Hardened oils have faced several problems. The technician at first looked upon them with distrust. The peculiar odor of these fats has caused considerable criticism and their surprisingly white color has been looked upon as unnatural. The soap produced with this stock has a characteristic structure and its appearance changes somewhat in storage. The distrust evidenced toward hydrogenated fat is shown, however, to be unjustified.

Hardened oils when used in soaps * in the proportion of 50 to 80 per cent give products which are very hard, dissolve with difficulty and do not lather readily. The saponification is also said to be somewhat slower than with ordinary soap fats. When about 30 per cent of hardened oil is used the soap is satisfactory.

Semi-boiled soaps were made as follows:

(1) 50 parts each of cocoanut oil and hardened oil were saponified at 80° C. with 38 degree caustic soda lye. The lye was stirred into the hot oil mixture and the kettle kept covered until a well saponified product was obtained. A little alkali was added to show a faint excess alkali by phenol phthalein. After short standing the soap was framed and cooled. It had a fine white color, but possessed a sharp odor (which however can be diminished or removed by boiling). The lathering qualities appeared less pronounced than was the case with a soap made from ½ tallow and ½ cocoanut oil. The hardened oil soap dissolved more slowly in water.†

(2) 80 per cent hardened oil and 20 per cent cocoanut oil saponified in the same way was very hard and white but showed no lathering properties. The odor was slightly rancid.

(3) 30 per cent hardened oil, 25 per cent peanut oil, 30 per cent cocoanut oil and 15 per cent rosin showed a rate of saponification which was normal; the soap was yellowish, the odor and solubility satisfactory, but the lathering properties were not quite as good as normal soap.

The conclusion reached with the hardened oils tested was that very hard soaps could be produced which would show great economy in use, that they gave a poorer lather, that there was some odor over and above that resulting in use of tallow, and that the saponification was slightly slower.‡ Hardened oils were also found to give dark

An example of a satisfactory soap base for toilet soaps is given in the following formula:

15 parts cocoanut oil,
45 parts tallow oil,
40 parts Talgol,

and suggestions are made for the manufacture of laundry soaps, white-grained soaps, cold process soaps, transparent glycerine soaps, soap powder, etc. The hardened fat is not suitable for the production of transparent soft soaps or natural grain soaps. (Seifenfabrikant (1912), 1229, 1257.)

* Seifen. Ztg. (1912), 660.

† Weber (Seifen. Ztg. (1913), 421) gives a somewhat complicated procedure for making soap base with hardened oils of the Talgol type.

‡ Leimdorfer (J. S. C. I., 1914, 206) states that the speed of saponification of hydrogenated fats is greater than the analogous natural fat (tallow) under similar conditions.

fatty acids by the Twitchell process and odor of the fatty acids was not regarded as entirely satisfactory.

A procedure for making milled soap base from hardened oil * involves the formula:

1200 pounds Talgol extra,
1200 pounds beef tallow,
600 pounds Ceylon cocoanut oil.

The tallow first was placed in the kettle and saponified with 20 degree caustic soda lye somewhat diluted with water. A little salt was added at the beginning of the boiling to prevent lumpiness. The Talgol extra was then added and saponified. This addition gave the stock a different odor which, however, diminished as the operation progressed and the final product possessed the desired odor of good neutral soap. After slow boiling for several hours the stock was allowed to stand over night after it had been ascertained that a sufficient excess of alkali was present. Subsequently the soap was salted out with 24 degree brine, and after settling the spent lye was replaced with 8 degree caustic soda lye. Slow boiling was continued for several hours to complete the saponification and improve the odor. After settling over night the lye was removed and the cocoanut oil, with the required amount of 30 degree caustic soda lye, was introduced. Less caustic soda was needed than the calculated amount for the cocoanut oil employed as the saponified stock contained some entrained lye. A small quantity of weak brine was added and boiling continued for several hours. Strong brine was then introduced to salt out the saponified product. After standing 36 hours the stock was withdrawn, solidified in cooling apparatus and subsequently dried. A relatively low temperature was used in drying yet no difficulty was experienced in securing a rapid removal of the moisture. The addition of hydrogenated oil to soft fats prevents adhesion of the resulting soap in the drying apparatus.

The soap base machined perfectly and yielded a first-class finished product. Samples of the soap were stored for several months and then given to unbiased persons for criticism without informing these judges that hydrogenated oil had been used in the make-up of the soap. All united in declaring the product an excellent one and the freshness of the perfume was noted. The lather exhibited by the milled soap was of a good stiff consistency and quite lasting, resembling that afforded by a shaving soap.

On examination, the glycerine-containing lyes derived in the fore-

* Seifen. Ztg. (1913), 334 and 368.

going method of saponification were found to resemble those obtained when beef tallow was used without additions of the hydrogenated fat.

Garth * states that a grained soap having a desirable hard feel may be obtained by the use of Talgol, as has been proven by practical experience. Also a larger yield is obtained, and since the Talgol products are cheaper than tallow itself, a double advantage is secured. The hydrogenated fat finds application not only in textile and laundry soaps but also in soap base intended for toilet soap manufacture. By itself Talgol is seldom used. In the case of laundry soap 25 to 30 per cent of rosin should be employed. As to shaving and transparent glycerine soaps, see Seifen. Ztg. (1913), 954. Too large an addition of the Talgol to grained soap causes the framed soap to check badly on standing.

Bergo † criticizes hardened oil from the point of view of soap making, stating that only a very moderate percentage of the hardened oil in conjunction with other oils and fats can be used, otherwise the lathering quality of the soap is seriously influenced. The somewhat musty odor which soaps containing 30 per cent or more hardened oil show, may be diminished or eliminated through long boiling, or by repeated washing, or by the addition of a suitable perfuming agent; but long boiling, as well as repeated salting out or covering the odor with perfumes, is costly. Another objection, namely, that soaps made with additions of hardened oil lose in lathering quality, is a more important consideration than the odor. The consumer looks upon good solubility and strong lathering properties as essential in soaps. Bergo thinks if success is not attained in removing this objectionable feature, the application of hydrogenated oils in the soap industry will remain very limited.

A further obstacle on a large scale is the color of the product obtained by autoclave saponification. Hardened oil, which as a neutral fat shows a beautiful white color, gives fatty acids which in spite of all possible precautions in the autoclave treatment and even with the use of bleaching material, such as decrolin and the like, appear of a yellow color and in consequence are not suitable for white soaps. If, he states, we do not saponify these oils for fatty acids, but process them as neutral fats and saponify with caustic alkali, then the difference in price as compared with other available fats and oils is so far reduced that it is a question whether the soap manufacturer will use such artificially hardened oils and thereby reduce the quality of the

* Seifen. Ztg. (1912), 1279.
† Seifen. Ztg. (1912), 1333.

soap. The hopes of the soap maker have been based on the supposition that a fat which would be a substitute in the manufacture of white grain soaps would be found, because the fats and oils now available for making white soaps are very few; while for yellow soaps a whole series of fats are obtainable and these Bergo regards as practically no more costly than hardened oil costs to-day. Hence he thinks these new raw materials offer no advantage for the soap industry in Germany on account of their price and defects mentioned.*

In contrast to the views of Bergo, a writer in Seifen. Ztg. (1912), 101, refers to the comment that hydrogenated fish oil gives dark unsightly soaps which do not show good lathering properties, and asserts that hardened animal and vegetable oils after careful boiling give soaps which not only are harder than those from the original oil, but are essentially whiter. If dark soaps have been produced, one perhaps can explain the failure on the ground that nickel soaps were present in the hardened oil and through sulfur compounds in the lye were converted into sulfide of nickel. The lack of lathering qualities of soap made from hardened fish or whale oil he contends is a perfectly natural result. Hardened fish oil finds its analogue in tallow. Pure tallow soaps are only indifferently soluble and lather poorly; hence this condition is to be expected in hardened fish oil.

Among a large collection of samples of soaps made from various hardened oils, including many marine animal oils, some were found to have a disagreeable odor like oil which has been distilled. This penetrating odor, which in distillation plants arises through partial decomposition of fatty bodies, is regarded as due to acrolein and is not a necessary consequence of hydrogenation, but is simply a result of over-heating the oil at some time during operation. In carrying out the process technically, too high a temperature should be avoided, thus eliminating the disagreeable odor and producing a hardened oil from which soap of high quality may be prepared. By the addition to hardened fish or vegetable oil of other fatty material, such as palm

* It should be remembered that in Germany the Leprince and Siveke Patent 141,029 is generally regarded as controlling, and is in strong hands. In consequence the criticism of hardened oil products by professional circles has been perhaps unduly severe, if not in part unwarranted.

Haleco (Seifen. Ztg. (1913), 16) feels that the stand taken by Bergo is unwarranted, because although the hardening of oils on a large scale has been in practical operation for only a short period, yet in that time there has been a very considerable demand for the hardened material, which demand is daily increasing in the soap industry and other fields. To-day soaps of various qualities, including fine toilet soaps, are being made with a considerable proportion of hardened oil which shows that the new material offers advantages.

kernel or cocoanut oil and rosin, a quick lathering soap may be prepared which satisfies all requirements.

Hauser * is of the view that the application of hardened oils in soap making is for the time considerably limited. It is not impossible that a considerable simplification of the apparatus will enable the soap manufacturers to make use of it more extensively. The more important applications, to Hauser, appear to be in the stearin and edible fat industry. He regards the soaps made from hardened fat as lacking in satisfactory texture and emulsifying properties, as not exhibiting the best of keeping qualities and in storage sometimes even developing an undesirable odor. Then, too, he considers the yield of glycerine to be unfavorably affected by hydrogenation and the fatty acids of hardened oil to be darker than those of the normal oil. In a modern soap establishment it is recommended that cheap, low-grade fat stock be the raw material, which, after purification, is split and the resulting fatty acids are distilled after hardening by treatment with sulfuric acid. In this way with great simplicity and certainty, according to Hauser, fractions of any desired titer may be obtained for various soap compositions without the occurrence of undesirable side reactions which he apparently thinks are unavoidable in hydrogenation processes.†

In the stearin industry the oil may be hardened and then saponified, or the glycerine first may be removed and the fatty acids hardened. It no longer becomes necessary to employ complicated pressing operations to separate stearin from olein as the stearin may be di-

* Seifen. Ztg. (1913), 141.

† Favorable comment of the Germania Oelwerke products is made by "R. D." (Seifen. Ztg. (1912), 517) who states that these hardened oils have many technical uses. In soap making they are used to advantage and give a good product. Talgol and Talgol extra are used as entire substitutes for tallow. Talgol is best for common household soaps, Talgol extra for toilet soaps. Candelite and Candelite extra on account of high melting point find advantageous application in the stearin and candle industry. He considers the odor of the hardened oils as slight and unobjectionable. The color is gray-yellow. Soaps made from these correspond to the trade requirements. Toilet soaps have a pure white color and do not darken or discolor on standing, and the perfume remains intact. Lower-grade soaps possess a satisfactory appearance, lather well and are sufficiently firm and the odor is satisfactory.

Considering the application of hardened fat in soap making Schuck (Soap Gazette and Perfumer, 1914, 55) states that on account of the high titer of the fat it is not advisable, in fact well nigh impossible, to make a settled soap (without rosin) from the hydrogenated product alone. Such a soap would be too brittle, would crack and would not lather at all.

Train oil (hardened) as a competitor of tallow is considered in Soap Gazette and Perfumer, 1913, 222. See also article by Heller, ibid., 1913, 263.

rectly obtained. The products to which he refers have the following constants:

	Talgol	Talgol extra	Candelite	Candelite extra
Iodine number	65–70	45–55	15–20	5–10
Melting point	35–37° C.	42–45° C.	48–50° C.	50–52
Saponification value	192	192	192	192
Unsaponifiable	under 1%	under 1%	under 1%	under 1%
Glycerine content	9–10%	9–10	9–10	9–10

A polemical article by **Ribot** * denounces the proposal to use hardened fish or whale oil, no matter how well refined, in the best grade of toilet soaps. Furthermore he does not consider such hardened oils to be substitute fats for tallow or palm kernel oil, but rather that the former may be employed as addition or filling-in fat stock. 20 to 25 per cent may be added to a cheap toilet soap base without detriment; 30 per cent or even 40 per cent may be employed in laundry soaps. In white soft soaps 40 to 50 per cent of Crutolin may be used.† **Schaal** ‡ apparently is in agreement with Ribot that for the highest grade of toilet soap base, tallow should not be materially reduced or displaced by Talgol, but maintains that a soap base may be prepared with 35 to 40 per cent of Talgol which yields a handsome milled soap permanent in quality and suffering no eventual change in color. He also asserts that for ordinary toilet soap base Talgol is in no sense an addition or filling-in fat, but is a real substitute for tallow, and that the same is true of Talgol extra and Candelite respectively for shaving soaps and glycerine transparent soaps; further that the hydrogenation process is an important and fruitful discovery for the soap industry, especially for toilet soap manufacture.

In "Eschweger" soaps tallow may be completely replaced by Talgol,§ which produces a firmer soap; the yield is good and the odor satisfactory and no objection has been raised to its lathering qualities.

* Seifen. Ztg. (1913), 142.

† In response to Ribot an article appeared in Seifensieder Zeitung (1913), 173, by Schaal in which the latter makes clear that he did not propose hydrogenated fish or whale oil of the Talgol type for making the very highest grade of soap base; he recommends such fats particularly for toilet soaps of medium quality. Schaal also states that he has never recommended complete substitution of tallow by Talgol fat in the highest grade of toilet soap base and calls attention to the formulæ which he has published in the past in which a substantial amount of tallow is specified.

‡ Seifen. Ztg. (1913), 173.

§ Seifen. Ztg. (1912), 1230.

Two formulæ are given for filled Eschweger soap according to which a firm marbled product is obtained.*

Transparent glycerine soaps may be prepared by the use of a hard variety of hardened oil, Candelite being especially suitable, and with this material a soap of very satisfactory transparent appearance and firm consistency may be prepared without using more than a normal amount of alcohol. The following are suitable formulas for the preparation of such soaps:

Cheap Grade

90 kilos Candelite.
90 kilos Ceylon cocoanut oil.
84 kilos castor oil.
144 kilos caustic soda lye, 38° Bé.
90 kilos sugar dissolved in an equal weight of water.
100 kilos soap filling.
30 kilos soda crystals.
Alcohol q.s.

The soap filling consists of 100 parts salt, 140 parts potash, 40 parts sugar and sufficient water to produce a solution of 21° Bé.

Better Grade

90 kilos Candelite.
120 kilos Ceylon cocoanut oil.
90 kilos castor oil.
166 kilos caustic soda lye, 38° Bé.
100 kilos sugar dissolved in 75 kilos of water.
40 kilos soap filling.
10 kilos glycerine.
Alcohol q.s.

The Candelite should first be melted, the cocoanut oil then added and finally the castor oil introduced. Saponification is carried out by the self-heating method, it being desirable to allow the saponified mass to stand an hour or so in order to assure a complete union of the

* "Eschweger" is a marbled soap, made by saponifying tallow and soft fats together with about one-third of their weight, or more, of cocoanut oil. The quantity of lye is gauged so as to have the soap very nearly neutral at the end of the operation, as there is no separation of waste lye. All that goes into the kettle also goes into the soap except of course water removed by evaporation. Owing to the properties of cocoanut oil, such soap, in absorbing a considerable amount of salt solution, becomes of a peculiar consistency, while hot, and crystallization ensues with the formation of "marble" or "mottle" on cooling in the frame. At the same time the soap holds much more water than one which has been mottled by boiling down a soap made entirely of soft fats.

ingredients. Then the sugar solution and filling are added. By proceeding in this manner a clear product is obtained which does not subsequently darken in storage. The amount of alcohol is usually about 3 to 4 per cent, calculated on the soap material. For the better quality a very satisfactory perfuming composition is obtained by mixing equal parts of " palma rosa " oil and artificial geranium oil using 1500 grams to the formula given above. For the cheaper grade of soap a good perfuming agent consists of a mixture of equal parts of Java citronella oil and benzyl acetate. 2000 grams of this mixture should be used for the amount of material specified in the formula first above given.*

Hardened oil is advantageously used in shaving soaps according to **Schaal.**† A formula given by him is the following:

50 kilos Talgol extra.
10 kilos Ceylon cocoanut oil.
10 kilos lard.
20 kilos caustic soda lye, 38° Bé.
21 kilos caustic potash lye, 37° Bé.

The mixing takes place at a temperature of 52° C. The lyes are first mixed and then added in a thin even stream, stirring well meanwhile in order to quickly get a thorough incorporation. After $\frac{1}{2}$ to $\frac{3}{4}$ hour the batch stirs thickly and should be promptly framed. The mass heats strongly in the frames and to take advantage of this the frames should be covered with bagging. By such treatment a section of the soap will show a uniform texture from center to edge.

If it is preferred to prepare this soap by the warm process, it is necessary to add 5 kilos of potash solution of 12° Bé. to the caustic lyes and to prolong the stirring until the mass has the proper body; the kettle is then well covered and its contents given time to react. After 2 to 3 hours spontaneous heating will have set in. The kettle is again opened, the contents well crutched, until uniform, and at the same time perfume can be worked in. The soap is now ready for framing, but the frames need not be covered. The potash solution is added to keep the soap sufficiently fluid to permit of crutching. Without this addition the soap would be so solid and tenacious that the crutch could scarcely operate. The finished soap has a flawless appearance, is almost white, fairly solid and handles well in cutting and packing.

* Schaal, Seifen. Ztg. (1912), 955.
† Seifen. Ztg. (1912), 954, and Die Moderne Toiletteseifen-Fabrikation.

A perfume composition which may be employed in this soap consists of the following:

200 grams oil of rosemary.
200 grams oil of bitter almonds (artificial).
150 grams oil of lavender.
75 grams oil of thyme (white).
100 grams oil of sassafras.
25 grams oil of wintergreen (artificial).

The odor and lathering properties of soaps made from hydrogenated oil are discussed by Garth * who considers the characteristic odor of hardened oils of the Talgol type to be in nowise disagreeable. In laundry soaps the aromatic odor of the rosin overcomes the Talgol smell. In making toilet soaps one has to take greater care that the Talgol addition is well gauged as otherwise the proportion of the customary perfuming agents has to be varied. With regard to the diminution of the lathering power he states that soaps from pure Talgol have almost no lather, and in this connection refers to the interesting work of Krafft and other investigators who have shown that the detergent action of soap is dependent upon the nature of the fatty acid, and that there exists an important difference in operation between stearin and olein soaps. Soaps from palmitin or stearin at common temperature are unworkable and develop their detergent or emulsion-forming properties only when a temperature is reached which is approximately that of the melting point of their fatty acids. On the other hand the olein soaps are soluble at ordinary temperatures thus exerting detergent action at low temperatures, but at a temperature of about 80° C. they lose their emulsion-forming qualities. Thus it will be seen why soaps made from pure tallow, or hardened fat, exert a very slight detergent action at ordinary temperature. In working with hardened fat the soap expert should take cognizance of the manner in which the soap is to be used and employ such materials as give the desired detergent property under these conditions.

With 30 to 35 per cent of hydrogenated oil of the Talgol type, **Weber** † has made a satisfactory soap base holding its perfume well, and although prepared without special manipulation did not, after standing for half a year, show the hardened oil odor when broken. This interval of time is sufficient to determine with certainty whether or not the characteristic odor can be permanently suppressed.

The fatty acids of hydrogenated oil have been examined by **Luksck** ‡

* Seifen. Ztg. (1912), 1309.
† Seifen. Ztg. (1913), 421.
‡ Seifen. Ztg. (1912), 718 and 742.

with reference to their applicability as candle material. A product having a titer of about 60 was observed to have a greasy feel, to be of amorphous texture and to be lacking in ring and transparency. So far as the samples examined by Luksch are concerned the product does not appear to be suitable as a candle material without considerable compounding.*

In saponifying for fatty acids it is not advisable to run above 92 per cent, as otherwise the fatty acids are likely to be dark and the resulting soap off color. When hydrogenated fish oil has been split the fatty acids are saponified in the customary way by carbonated alkali. In finishing, the soap should not be too thin; otherwise, in spite of the high melting point of the hardened fat, the soap will be soft. The soap should be separated only with an excess of lye. It separates rather badly and should be allowed to stand two or three days in the kettle in order to harden. A soap made from Talgol with 30 per cent of rosin is of fair appearance, lacking, however, the transparency of soap prepared with a large content of palm kernel oil. While the color is good, there is a noticeable dullness of surface. After drying and pressing it acquires a satisfactory glossy finish. While a soap made only from hardened fish or whale oil has practically no lathering properties, the addition of 30 per cent of rosin greatly improves this defect and very good lathering properties result.†

* Even if it were possible, "J. G." states (Seifen. Ztg. (1912), 1146), to split the fat completely on a commercial scale, the color of the fatty acids excludes the direct application of the product in candle manufacture. He even claims that it is necessary to subject the saponified product either to distillation or to pressing, and that in the latter case the poor crystallization of the fatty acids gives rise to difficulties. But he adds that the ordinary stearin candle is made up largely of a mixture of palmitic and stearic acid in which a certain ratio between the two fatty acids must exist to maintain the quality of the candle. Hence in judging hardened fat with reference to its application as a candle material, the composition of the original fat is not unimportant, for useful mixtures may well be obtained through careful selection of the raw materials. In those cases where the nature of the chemical individuals derived by hydrogenation have not been entirely made clear, as in the case of fish and whale oil, further practical investigations will be necessary to show whether or not hydrogenation will afford a generally useful product in candle manufacture.

† Seifen. Ztg. (1912), 870.

A few years hence when oil hydrogenation has found its measure and the more important points concerning it have reached definite settlement, the allotment of space to a number of the discussions appearing in this chapter hardly would be warranted, but at the present time when many are desirous of having at hand a review which comprises all or nearly all the published work to date, containing though it does a considerable divergency of opinion, there appears ample justification for the inclusion of such discussions as those given above.

A tallow-like product which has been brought into the market as "Talgit" is prepared by hydrogenating fish or whale oil. **Müller** has examined this product * and has reported the acid number as 12.8 and the iodine number as 49. The fatty acids exhibited a titer of 39.4° C. When Müller attempted to saponify the fat by the Twitchell process, dark colored fatty acids were produced, caused, it is supposed, by oxidation during saponification. Müller observes that copper, iron and lead tend to cause a discoloration of fat which is treated by the Twitchell process, and he concludes that the traces of nickel which were present in Talgit acted in a similar manner. When he subjected the fat to cleavage by the autoclave process very light colored fatty acids were obtained. A pressure of 10 to 11 atmospheres was maintained in the autoclave for a period of 8 hours and the resulting fatty acids were found to contain about 2.5 per cent of unsaponified fat. The following results were obtained from an examination of the fatty acids:

Acid number of the fatty acids	194.0
Saponification value of the fatty acids	198.0
Titer	39.2° C.
Acid number of the liquid fatty acids	186.3
Saponification values of the liquid fatty acids	191.2
Iodine number of the liquid fatty acids	100.0
Titer of the liquid fatty acids	14.3° C.
Titer of the solid fatty acids	48.7° C.

The fatty products of the saponification pressed very readily and about 35 per cent of solid fatty acids were obtained whose low titer (48.7° C.) indicates, according to Müller, that fatty acids in addition to or other than stearic and palmitic acids are present, for the solidifying point of mixtures of palmitic and stearic acids is above 53.5° C. The presence of iso-oleic acid which causes a lowering of the titer of stearic acid obtained by distillation is not to be expected in this case, but Müller has not further investigated the acid mixture to identify any of its components. As the fatty acids pressed satisfactorily, Müller concludes that the stearic acid was technically pure, hence the low titer cannot be ascribed to the presence of undue amounts of liquid fatty acids. The expressed fatty acids, or oleic acid, obtained as stated above, exhibited a straw yellow color and showed the characteristic odor of hardened fish or whale oil. Müller states that for many purposes the iodine number of these liquid fatty acids is too high. He concludes that so far as this product is concerned the hydrogenation of the unsaturated fatty acids does not proceed successively

* Seifen. Ztg. (1913), 1376.

so as to convert all of the unsaturated bodies having two or more double bonds into bodies having only one double bond before the latter bodies are hydrogenated, or in other words that linoleic and linolenic acids are not all converted into oleic acid before stearic acid forms, but instead of this that reduction takes place throughout, so that all types of unsaturated compounds are more or less reduced simultaneously. This observation is of interest because, as Müller notes, the presence of highly-unsaturated bodies of the nature of drying oils in such products is often undesirable.

Müller prepared soap from Talgit and found it to have little or no detergent and lathering properties which he notes is to be expected with fats of this titer, and in consequence of these properties, products of the nature of Talgit cannot be used as the essential fat material, but should be used only as additions to the main fat stock.

Commenting on the observation of Müller regarding the properties of Talgit, Dubovitz (Seifen. Ztg. (1913), 1445) notes that the investigation of the fatty acids of hardened fish oil indicates that there is present an acid whose molecular weight is less than that of palmitic acid. Also it is stated that it is possible to obtain stearic acid or stearin having a titer of 53 to 55 degrees from strongly hardened fish oil simply by pressing.

Müller (Seifen. Ztg. (1914), 8) discusses the comments of Dubovitz and points out that mixtures of two saturated fatty acids crystallize well from the stearin manufacturer's point of view, while mixtures of three or more fatty acids as a rule produce an amorphous mass.

The contention of Dubovitz that the low titer of stearin can be explained by the presence of saturated fatty acids with less than 16 carbon atoms in the molecule and derived from the corresponding unsaturated compounds by hydrogenation rests on the assumption of the existence of just such unsaturated fatty acids, or their glycerides, in fish oils. Proof of this is said to be lacking up to the present. Even the presence of hypogeic and physetoleic acids in these oils is still doubted. It is held that the low titer of the stearin in question was due to the presence of unsaturated fatty acids. (Seifen. Ztg. (1914), 33.)

In discussing the distillation of fatty acids, **Hajek** * states that some difficulties are encountered when working up hydrogenated oils to produce fatty acids. He states that all fats which are treated when hot with air or other gases for a considerable length of time, after autoclave saponification, yield dark colored fatty acids and that this discoloration is due to a chemical change which takes place in coloring agents present, similar in character to that which occurs in the distillation of fatty acids at elevated temperatures, or with an insufficient proportion of superheated steam.†

* Seifen. Ztg. (1913), 445.

† The idea which has been entertained that hardened triglycerides could be directly used for candle material is out of question, as no one would care to inhale the vapors

Normann has made candles with stock obtained from hardened fish or whale oil which burned brightly and without odor, similar to the best grade of stearin candles.*

The properties of hardened castor oil have been noted by Garth.† As is generally known, castor oil differs in many respects from other common oils in such respects as its high viscosity, solubility in alcohol and difficulty of salting out its soaps by electrolytes. The constants of one sample examined by Garth are as follows:

Acid number	3.5
Saponification number	183.5
Iodine number	4.8
Acetyl number	153.5
Acetyl number of the fatty acids	143.1
Acid number of the fatty acids	184.5
Saponification number of the fatty acids	187.9
Melting point of the fat	68° C.
Melting point of the fatty acids	70° C.
Melting point of the acetylated acids	47° C.

These results indicate that the saponification and acetyl number do not change. The difference between the acid number of the fatty acids and their saponification number points to the formation of lactones.

From the point of view of soap technics, it may be noted that the hardened product saponifies with dilute lye about as easily as common

coming from candles in which acrolein was being generated. Any large proportion of nickel in the fat would also interfere with the burning qualities. (Sach, Zeitsch. f. angew. Chem., 1913, No. 94, 784.)

The slight lathering properties of soap made from hardened tran is to be expected, because this fat finds its analogue in tallow. Pure tallow soaps are very difficultly-soluble and lather very poorly so the same property may be looked for in hardened fish oil or whale oil. (Seifen. Ztg. (1912), 1003.)

The dark colored soaps which have been noted by some users of hardened oil may be due to traces of nickel soap in the oil which react with sulfur compounds in the lye, resulting in the formation of nickel sulfide and consequent discoloration. (Seifen. Ztg. (1912), 1003.)

The odor of hardened tran is very much like that of distilled oils and recalls the penetrating disagreeable odor which is observed in distillation works and which is apparently due to the partial decomposition of fatty acids with the production of acrolein bodies. Odors of this character materially affect the quality of the soap, but this trouble may be avoided if greater care is taken in the hardening process to avoid over-heating of the oil or fat. By skillful working at not too high a temperature, the disagreeable odor does not appear and the tran is rendered completely odorless. From this product a soap may be made which is beyond criticism.

* Seifen. Ztg. (1914), 263.

† Seifen. Ztg. (1912), 1309.

castor oil. Further, soap prepared from the hardened product, in spite of its high melting point, like castor oil soap, has a similar lack of sensitiveness against salt solutions and behaves in this respect like the fats of the cocoanut oil group. Like the fats of the latter group, the hardened fat may be saponified at a temperature of about 80° to 90° C. While a soap with 30 per cent fat content made from ordinary castor oil is liquid, the corresponding soap from hardened castor oil is very firm, but the latter soap does not possess the property of lathering in the least.

With regard to tariff rating on hardened oil **Böhm** * thinks beyond question the hydrogenated product should not be declared and rated like the untreated oil and draws an analogy between raw oils and their hydrogenated products and formaldehyde or acetaldehyde which yield chemically different bodies, respectively methyl and ethyl alcohol, by taking up hydrogen.

It is contended † that Böhm's illustrative use of formaldehyde, which body through the addition of two atoms of hydrogen is transformed into methyl alcohol and thus into an essentially different body from the tariff point of view, is not entirely analogous with respect to hardened oils, for oils are not unitary chemical individuals, but are mixtures of triglycerides of various fatty acids. Also it is held that hydrogenated oils are not essentially single chemical individuals like tristearin, but are mixtures of various fatty acid triglycerides in which mixtures, of course, tristearin is present in much greater quantities than in the original oil. A differentiation for tariff purposes on the ground of chemical composition is thus practically impossible.‡

Dr. Bela Lach, in the Seifen. Ztg. (1912), 1245, discusses American soap manufacture and refers to the Fels Naptha Soap Works of Philadelphia, as being users of hydrogenated oil. He says that Fels Naptha soap contains from 10 to 15 per cent of benzene of high boiling point, and that the raw materials are in a large part cotton and corn oil. Only a relatively small proportion of hard stock, such as tallow or

* Seifen. Ztg. (1912), 738.

† Seifen. Ztg. (1912), 1003.

‡ An article by Harmsen (Seifen. Ztg. (1913), 638–39 and 661–62) discusses the matter of tariff adjustment of hardened fats, and he states that by the hardening operation the consistency and other qualities of the oil are so modified that a recognition of its origin is in most cases impossible either by taste, smell or chemical test. Chemical analysis can determine only whether the fat is of animal or vegetable origin. The Hamburg authorities have arrived at the conclusion that hardened fat or oil must be taxed according to the properties and quality acquired by hardening. Harmsen also discusses the position of Talgol from the tariff standpoint in Seifensieder Zeitung (1913), 745.

palm kernel oil, is used. The amount of this material employed is, however, reduced because this concern has been able to make use of hydrogenated oil, a material which they have thoroughly tested. At this plant Lach states he saw samples of hardened cotton and corn oil, as well as various kinds of hardened fish oil which were of a remarkably fine character. They had the hardness and appearance of fine tallow, were beyond criticism as to odor and could be worked up into a soap in a satisfactory manner.

A hardened oil of relatively low titer, bearing the trade name of "Krutolin" (or Crutolin),* is discussed in the Seifensieder Zeitung (1913), 930 and 954, and as some of the observations may be of use in the handling of other more or less similar hydrogenated products the following data is here included.

On account of the great demand for good fats and oils in edible-fat manufacture, the prices of these have increased very materially, and it has become continually more difficult to obtain fats which remain white on boiling. Therefore hardened oils such as Krutolin, which may be obtained of uniformly good quality, promise to be of decided utility. It is said that Krutolin has the advantage of being cheaper than lard and cottonseed oil, and that in addition it is, as has been proven by long-continued experiments, a good substitute for lard and white cottonseed oil. When used for barrel soaps, Krutolin, alone, has a tendency to form sirupy, stringy soaps. Therefore, it is desirable to supplement it by the proper addition of other fats. In practice it has been shown that the danger of "lengthening" of *unfilled* white soft soaps is greater than when more or less potato flour is used as a filler. Hence it is recommended that the percentage of Krutolin employed be kept somewhat lower for such unfilled products.

As mutton tallow, cottonseed oil, peanut oil and lard, or their fatty acids, in Germany are the usual or principal raw materials for white soft soap, it is stated that under present market conditions a considerable saving is attained in the manufacture of soaps if these fats are replaced, even only in part, by Krutolin. In combination with the above-named raw materials Krutolin furnishes a very white soap for both unfilled or filled goods. It is self-evident that a primary condition for the production of a totally white soap is cleanliness of working. Furthermore, it is necessary to pay attention to the alkali and especially the potato flour as these are often of varying origin, and are not always suitable. Many 50-degree caustic potash lyes give perfectly water-white solutions when diluted; others, however, show a yellow tone. With filled soaps the quality of the potato flour has a strong influence on the character of the finished product. Every shipment should be tested for color and to ascertain whether the flour has been treated with acid. Potato flours containing acid are to be excluded for filling white soft soaps, as they produce an after-darkening. The kind of water used also has some influence on the color of these soaps.

A stock for unfilled figged soap containing Krutolin follows:

1500 kg.	mutton tallow
900 kg.	cottonseed oil
600 kg.	Krutolin
3000 kg.	

On account of the high titer which mutton tallow possesses and in recognition of the fact that Krutolin easily favors the "lengthening" of the soap, one must

* Krutolin is stated to be a substitute for "technical" lard and American cotton oil (Seifen. Ztg. (1913), 1386).

from the beginning count on a strong increase of carbonated alkali to reduce the causticity of the caustic potash lye. It is possible, in the above stock, to use 30 kg. 96 to 98 per cent potash to 100 kg. of 50-degree caustic potash lye. It will often be advisable, especially during the warm season, to substitute ammonia soda solution for a part of the potash solution, in order to secure an easy and rapid figging of the soap.

After completion of the boiling, samples are to be carefully tested to ascertain if the soap has been sufficiently shortened by carbonated alkali. Samples placed on glass must remain liquid a long time, and on stirring after cooling must not show any stringiness. Should the soap still remain tough and gum-like a later addition of concentrated potash or soda solution is necessary in order to produce a satisfactory product. On account of the large amount of carbonated alkali which can be absorbed, the yield of this soap is very good.

The mutton tallow can be omitted and a somewhat larger amount of white lard substituted. The composition would then be about as follows:

1600 kg.	lard
750 kg.	cottonseed oil
650 kg.	Krutolin
3000 kg.	

As lard has a considerably lower titer than mutton tallow, the amount of shortening material used with this stock must be decreased accordingly. With the stock first given, which contained a large amount of mutton tallow, additions of caustic soda lye were not necessary, but in this case, where softer fats form the basis, it is advisable to add about 20 per cent of caustic soda lye in the boiling. The neutral fats in this stock can be replaced by fatty acids, but as soaps from neutral fats are whiter, this is not to be recommended. A moderate filling with flour is advantageous when using fatty acid stock. A figged soap with a little filling can hardly be distinguished by visual examination from one which is unfilled. For the above stock of 3000 kg. the following filler is recommended:

300 kg. best potato flour.
600 kg. 12-degree potash solution.
300 kg. lye, 30° Bé.

The filler is to be added in the morning if the soap has cooled sufficiently over night. The soap is perfumed with sal-ammoniac, turpentine, safrol, oil of camphor, lemon oil or suitable mixtures of these.

For a first-class "sal-ammoniac-turpentine" soft soap, where particular value is laid upon the resulting white color, and less on the figged effect, mutton tallow and cottonseed oil may be left out and Candelite and Talgol substituted in part therefor. The composition would then be the following:

2000 kg. Krutolin.
1000 kg. Candelite.

For the reduction of the causticity 30 kg. potash should be used to every 100 kg. 50-degree caustic potash lye. On boiling about one-third caustic soda is to be added. To the latter 25 kg. ammonia soda are added to every 100 kg. soda. These alkalies are dissolved separately, mixed and the lye diluted to the required strength.

The above stock gives a soap of special toughness. Therefore, it may be necessary to add more or less soda or potash solution according to the result of tests made from time to time, until the soap possesses the desired normal characteristics. "Sal-ammoniac turpentine soap" made according to this formula possesses a very white

color and by use of first-class potato flour can be filled up to 25 per cent without influencing the color.

The filler is made up as previously mentioned, but must have an addition of potash filler. Its make-up thus becomes:

750 kg. potato flour.
1500 kg. 12-degree potash solution.
375 kg. potash filler.
750 kg. 30-degree "take-off" lye.

In order to more surely prevent the lengthening of the soap ammonia-soda solution also may be used in part in the filler instead of potash solution. For second and third quality soap which can be filled in a similar manner with 50 and 75 per cent of potato flour, the formula and boiling remain the same. These filled "sal-ammoniac turpentine" soaps should be perfumed rather strongly with sal-ammoniac and some turpentine, for prospective purchasers judge the soap not only by its white color, but also by the more or less strong ammoniacal odor.

As already mentioned, the yield of such soaps is said to be increased by the use of Krutolin. This is explained by the increased ability to take shorteners. For example, a "sal-ammoniac turpentine" soap filled with 50 per cent potato flour, gave a yield of about 250 per cent.

Krutolin is not available for natural grain and green soft soaps, as here its qualities do not make it a substitute for either tallow or linseed oil. Tallow is necessary for natural grain soaps; at least up to now it has been impossible to produce a faultless grain formation with Krutolin or Talgol. Krutolin is also not suited for a perfectly clear transparent soft soap.

From long continued tests in a large way it has been shown that Krutolin can also be added to the stock used in making bar soaps, insuring light color with good pressing qualities.

A stock giving a light yellow soap which presses well, is the following:

1200 kg. Krutolin
1200 kg. fatty acids of Talgol
300 kg. fatty acids of by-product cocoanut oil
300 kg. fatty acids of palm kernel oil
3000 kg.
450 kg. rosin = 15 per cent
3450 kg.

Under normal treatment and good cooling the above stock will furnish a soap of adequate firmness. Of course, the amount of rosin added has an important influence on the solidity of the soap. With large amounts of rosin the use of soft fats must be minimized, as otherwise there is danger of obtaining too soft a soap in spite of the cooling treatment.

A stock with 20 per cent rosin has the following composition:

800 kg. Krutolin
600 kg. fatty acids of light bone fat
1000 kg. fatty acids of Talgol
300 kg. fatty acids of by-product cocoanut oil
300 kg. fatty acids of palm kernel oil
3000 kg.
600 kg. rosin = 20 per cent
3600 kg.

To obtain sufficiently solid soaps it is important to separate sharply on salting out so as to secure a good grain. By doing this the appearance of cake soap may be somewhat marred. This, it is further stated, is not to be feared so much with cooled soaps, as undesirable segregation cannot occur to any material extent during the rapid solidification. This is one of the main advantages of cooling machines in addition to the rapid production of goods ready for shipment. If only by-product cocoanut or palm kernel oil from edible fat manufacture are to be used for the stock instead of the best palm kernel fatty acid, it will be necessary to reduce the proportion of rosin as the resulting soap may otherwise be too soft. These by-product cocoanut or palm nut oils almost always contain sesame or other similar oils, and influence the soap produced from them. When Krutolin is used in this manner it is advisable to perfume with safrol, lemon oil, etc., before cooling in order to cover the peculiar odor of this raw material which is disagreeable to some people.

For settled yellow rosin grain soaps Krutolin can also be used to advantage as it improves the base for later coloring. The action of crude palm oil used for coloring will be materially stronger with a clear soap base, than if, for instance, dark bone fat has produced a base difficult to cover.

The composition of the stock is the following:

600 kg.	by-product cocoanut oil
900 kg.	Krutolin
600 kg.	fatty acids of light bone fat
450 kg.	fatty acids of Talgol
450 kg.	crude palm oil
3000 kg.	
600 kg.	rosin = 20 per cent
3600 kg.	

Here also the condition of the finished soap must be the regulator for its composition. For instance, if the soap is too soft, the percentage or rosin or Krutolin is to be reduced.

Krutolin also finds a use in making white wax grain soaps and various grades of textile soaps. Where the kind and color of the soaps allow, as has been repeatedly found with textile soaps, Krutolin should be split, in order not to lose the glycerine.

Krutolin can be used to advantage as an addition fat in making soaps by the cold process, although care should be taken in its use. With unfilled toilet soaps about 30 per cent Krutolin may be used with about 70 per cent of cocoanut oil. If the soap is to be filled, the percentage of Krutolin should be correspondingly reduced, since otherwise the soap would suffer in appearance and would be poorly bonded.*

In preparing a white soft soap Bergo (Seifen. Ztg. (1913), 1220) uses 1000 kg. fatty acids of cotton oil to 200 kg. of Candelite. 900 kg. of 30° Bé. caustic potash lye and 300 kg. of 25° Bé. caustic soda lye are used together with 100 kg. of carbonate of soda lye of 30° Bé. The caustic potash lye is reduced with carbonate of

* Seifen. Ztg. (1914), 8.

potash solution. The lyes are put in the kettle first, the fatty acids slowly added and then the Candelite.* (Chem. Abs. (1914), 588.)

Hydrogenated linseed oil has been put on the market under the name of "Linolith" by the Germania Ölwerke.† Two grades are manufactured. One grade has a melting point of 45° C., and the other melts at 55° C. Both grades show a saponification number of 188 to 195 and a glycerine content of 9 to 10 per cent. Linolith has not been used extensively in white soaps as it is off color, but is serviceable for the preparation of rosin or "Eschweger" soaps and the like. While the raw material, linseed oil, is liable to cause yellowing or after-darkening of soaps or the sweating out of drops of a yellow liquid, the hardened oil is thought to be free from these objections, but caution is advised in its use until thorough tests have been carried out.‡

Soaps made with hardened linseed oil (Linolith) and rosin are of good quality and the odor and color are excellent.§ The following formulæ have been tested:

* The character of soaps made from hardened oil in conjunction with cottonseed or peanut oil is discussed in Der Seifenfabrikant (1913), 31.

† Talgol, Candelite, Krutolin and Linolith have taken a place in the German market and are listed among the fats regularly quoted. (See Seifen. Ztg. (1913), 1386.)

In Germany the price of fish and whale oils fluctuates to some extent with that of linseed oil by reason of the demand for these oils by oil-hardening concerns. (Seifen. Ztg. (1913), 1385.)

Linseed oil is in increased demand for the manufacture of hardened oils and edible compounds. It is stated that in North America this oil promises to become an important raw material for the hydrogenation industry. (Seifen. Ztg. (1913), 1277.)

R. H. Adams, president of the American Linseed Company, attributes considerable importance to the hardening process as applied to linseed oil. "The hydrogenation process," Adams states, "is merely in its infancy and is bound to exert a powerful influence upon the oil markets, and will prevent the price of linseed oil from ever going to the low levels which have been reached in certain years of the past." He states that the process would not affect linseed oil alone, but as the process was applicable to other vegetable oils and to fish oils, the question of comparative prices would largely determine the extent of consumption in the case of each oil. The increased outlet for linseed oil afforded by virtue of the hydrogenation process was generally credited to the soap trade. While consumption of oil for soap-making purposes undoubtedly has increased, Adams states that another outlet, and one which may assume very large proportions, is found in the edible trades, and even now large quantities of linseed oil are being thus consumed on the Continent. (O. P. & D. R., March 10, 1914.)

‡ Seifen. Ztg. (1913), 1299.

§ Seifen. Ztg. (1914), 231.

	A	*B*	*C*	*D*
Linolith, M. P. 45° C., or its fatty acids..	1600 lbs.	1600 lbs.	....	....
Linolith extra, M. P. 55° C., or its fatty acids..............................	....	....	1500 lbs.	1500 lbs.
Fatty acids of palm kernel oil...........	400	200	400	300
Fatty acids of cocoanut oil...............	....	200	....	....
Fatty acids of peanut oil.................	....	300	500	500
Fatty acids of Talgol.....................	500	....	300	....
Soft fat....................................	500	700	300	700
Rosin.......................................	750	1050	900	1200

The fatty acids were saponified with carbonate and the neutral fat with 30 degree caustic soda. The Linolith extra was found capable of carrying a higher proportion of rosin than the regular Linolith.

Linolith does not exhibit any marked odor such as is observed in the case of much of the hardened fish oil on the market and is regarded as suitable for the manufacture of white grained soaps.* The following procedure has been tried and a satisfactory product obtained. 50 parts of Linolith, 10 parts of a tallowy fat and 40 parts of fatty acids derived from a vegetable oil were employed. The Linolith and tallowy fat were saponified and it was noted that saponification progressed rapidly. The product was bleached with Blankit and salted out. After settling it was combined with stock derived from the separate saponification of the vegetable oil, and well boiled and salted out. The soap was duly grained and afforded a product of excellent feel and good odor. The color was not a pure white.

The difficulties in using hydrogenated linseed oil (Linolith) in white-grained soaps, according to Wilhelmus,† have been that the color was not sufficiently light and the lathering properties were deficient. The texture of the soap was unsatisfactory and cracks occurred on standing. In investigations directed toward the elimination of these objectionable features Wilhelmus found that much depended on the manner of cleavage of the hardened linseed oil. While with autoclave treatment saponification to the extent of 88 to 90 per cent gave fatty acids of good color, it was not found feasible with the Twitchell reagent to exceed 80 to 82 per cent, as the resulting fatty acids otherwise were too dark for white soaps. Pfeilring reagent afforded better results and Wilhelmus regards this cleavage compound to be of specific value in splitting hardened oils. Benefit is derived by adding to hydrogenated linseed oil a quantity of an oil, such as peanut oil, which splits easily, yielding light colored fatty acids. By subjecting the hardened oil to cleavage under these conditions a better grade of fatty acid may be obtained.

* Seifen. Ztg. (1914), 140 and 167.

† Seifen. Ztg. (1914), 257.

In making the soap about 40 per cent of hydrogenated linseed oil (Linolith) may be employed. After saponification with alkali and graining in the kettle, the product is bleached. For this purpose a bleach consisting of 91 parts of water, 5.8 parts of sodium bisulfite, 2 parts of sulfuric acid and 1.35 parts of zinc dust are used for 1000 parts by weight of the fat. The use of soap-cooling apparatus, in place of frames, enables a better control of the color. The addition of 10 to 15 per cent of castor oil improves the solubility and lathering qualities of the soap. 15 per cent of castor oil is the maximum.* If still higher lathering properties are required "Saponin" powder may be added.

* The preparation of soaps with fatty mixtures consisting of saturated fats, such as those derived by hydrogenation, with unsaturated fats or oils has been made the basis of an application for German Patent by Worms and the novelty of the idea is criticized in Seifensieder Zeitung, 1914, 392.

CHAPTER XI

HYDROGENATION PRACTICE

Whether or not the plant is to treat animal or vegetable oils, or fish oil, the following general procedure may be laid down for guidance in the equipment and operation of a hydrogenating works.

The starting point is, perhaps, the preparation of catalyzer. Of course the procedure employed for its preparation depends on the type of catalyzer selected. Suppose nickel be chosen as the active material, to be used on a suitable carrier or supporting base. To this end a solution of a nickel salt, such as the nitrate or sulfate, is mixed in vats with the support, in the presence of a precipitant, or the latter is subsequently added, and the material is well agitated. Soluble salts should then be removed by washing and the material dried. These operations may take place in a filter press supplied with air under pressure. The caked product should be ground in a ball or pebble mill until resolved into a fine powder.

The catalyzer is now ready for reduction, which should be performed with extreme care as the entire oil-hardening process depends on the efficiency of the catalyzer. A simple and efficient type of catalyzer-reducing device is represented by Fig. 55. *A* is a brick structure which contains the reducing drum *B*. The latter is rotated by means of the sprocket *C*. E^1E^2 are stuffing boxes which admit of rotating the drum without disturbing the gas inlet and outlet. The catalyzer is admitted and withdrawn through the gate *G*. The drum is filled about two-fifths full of the catalyzer and hydrogen passed in. When tests for oxygen show that all the air has been expelled the drum is heated to a temperature not exceeding 360° C. During reduction the hydrogen is passed through at a considerable rate in order to remove the steam formed, thus reducing the partial pressure of the latter and facilitating the reduction of the nickel oxide or hydrate. The gases issuing from the exit side of the drum may pass through a water seal and after purification may be returned to the gas holders to be used again. When the issuing gases are found to contain no steam the reduction is complete, the heating is discontinued and the catalyzer allowed to cool in a current of hydrogen.

After cooling the catalyzer, the hopper shown in Fig. 55 is coupled to the flange of the gate *G*. The bottom of the hopper dips below the surface of oil contained in a receptacle beneath. Hydrogen is passed in at the valve *J* and the air is thereby expelled from the hopper. The valve of the reducing drum is now opened and the catalyzer allowed to fall into the oil with which it should be thoroughly mixed. Thus the catalyzer is effectively sealed from the air.

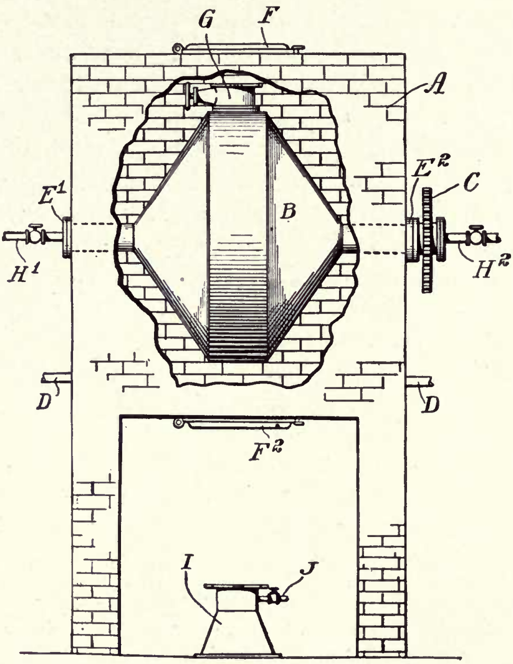


Fig. 55.

This method of abstracting catalyzer from the reducing drum prevents oxidation of the nickel which occurs to a greater or less extent when the catalyzer is withdrawn in contact with the air.

The catalyzer in oil may then be transferred to a large agitating tank in which oil is added in sufficient quantity to make the mixture contain the correct percentage of catalyzer. The contents are thoroughly agitated and transferred to the hydrogenator where the actual hydrogenation takes place.

Tall iron tanks may be used for this purpose, one type of which is shown in Fig. 56. The air in the hydrogenator is displaced by means of hydrogen and the mixture of catalyzer and oil pumped from the

agitator *A* into the hydrogenator *C*. The contents of the hydrogenator are heated to a temperature of 175° to 190° C. by means of superheated steam or hot oil coils, the latter being preferable owing to the danger of leakages of steam into the chamber. The temperature of the contents of the hydrogenator should be registered by means of a reliable thermometer, preferably a recording pyrometer.

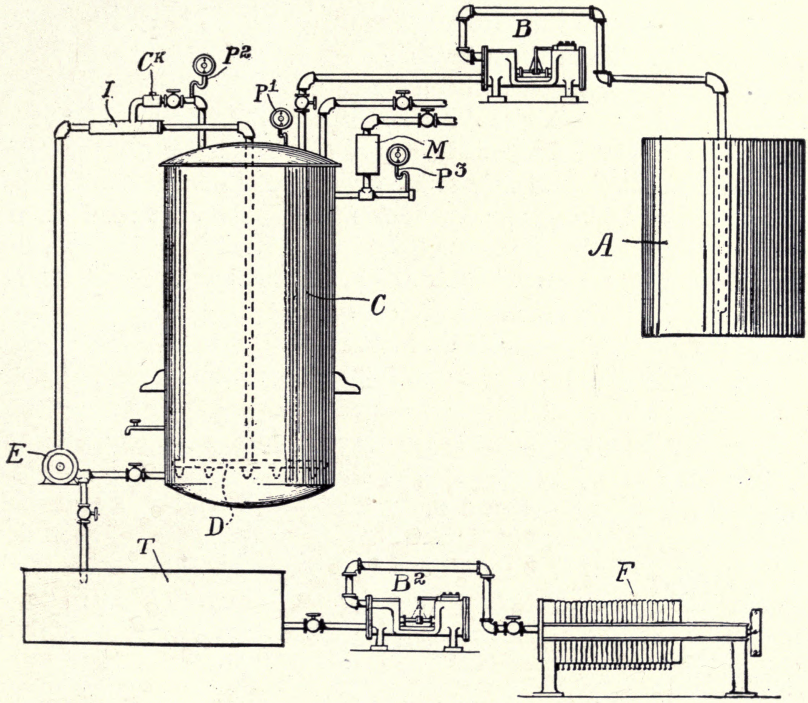


FIG. 56.

The oil and catalyzer in the hydrogenator are circulated by means of the rotary pump *E*, which takes the liquid from the bottom of the hydrogenator and pumps it through the inductor *I* where hydrogen drawn from the gas space at the top of the hydrogenator is mixed with the oil. *CK* is a check valve to prevent oil from entering the tank through the suction tube in the event of the inductor suction nozzle becoming flooded. The mixture of oil, catalyzer and hydrogen is ejected through the distributor *D* at the bottom of the hydrogenator.

The hydrogen inlet is provided with a safety device *M* and a pressure gauge P_3.

The pressure maintained in the hydrogenator is variable according to the oil under treatment and may range from atmospheric or less up to about 25 pounds.* The difference in the readings of the pressure gauges P_1P_2 registers the suction of hydrogen at the suction nozzle of the inductor. Samples of oil may be withdrawn from time to time from the outlet Q. When the sample indicates that the oil has the required hardness the hydrogenator is emptied through the outlet V and the contents are run into large tanks which are heated by means of steam coils. From these tanks the mixture of oil and catalyzer is pumped into filter presses where the catalyzer is removed. The oil is finally run into cooling tanks where it solidifies to a hard fat ready to be made into lard compound, soap or other product.

The transformation to olein of the glycerides of linoleic and linolenic acids or other highly unsaturated acids usually does not result in any marked change in the titer. As these bodies sometimes are, to a considerable extent, transformed into olein before olein becomes stearin, hydrogen will be absorbed by the oil without hardening, to a degree dependant on the proportion of these highly unsaturated bodies present. Often an hour or more is needed to bring an oil to the "olein stage," after which hardening will progress rapidly.

Of course, the method given above is capable of many modifications, as oils of different character require different treatment and in consequence oftentimes call for equipment which varies considerably from that given by way of illustration. Catalyzers vary a good deal in their properties, and conditions which are suitable for nickel in some of its forms will not answer for palladium. A much lower temperature usually suffices when using the latter metal as a catalytic substance.†

* One of the difficulties met with in the handling of hydrogen has been the loss by leakage of the gas. Under pressure and at a temperature of 150° or 200° C., hydrogen is surprisingly penetrating. Autoclaves with welded seams are desirable for high-pressure and high-temperature work. Moving parts should be avoided as far as possible.

† Reference is made to the chapter on catalyzers which gives much detailed information on the subject. Attention is, however, called to the existence of several patents covering certain forms of catalytic preparations.

CHAPTER XII

THE HYDROGEN PROBLEM IN OIL HARDENING

Oleic acid and hydrogen combine, molecule for molecule, to yield stearic acid according to the reaction:

$$C_{18}H_{34}O_2 + H_2 = C_{18}H_{36}O_2.$$

Thus 282 pounds of oleic acid require 2 pounds (or about 0.7 per cent) of hydrogen for the production of 284 pounds of stearic acid, and similarly the transformation of olein into stearin requires the use of about 0.68 per cent hydrogen.*

One thousand cubic feet of hydrogen weigh approximately 5.6 pounds, hence a pound of olein calls for a little over 0.1 of an ounce of hydrogen equivalent to approximately 2500 cubic feet of hydrogen per ton (of 2000 pounds) of olein. Thus by weight only a relatively small quantity of hydrogen is needed, while by volume the amount required, of course, is considerable.†

* The amount of hydrogen required for complete conversion is given by Sachs (Zeitsch. f. angew. Chem., 1913, 94, 784) as 7.4 kilos or 85 cubic meters hydrogen per 1000 kilos oleic acid. 1000 kilos of linoleic acid having two double bonds call for 14.2 kilos, or 170 cubic meters of hydrogen. 1000 kilos of linoleic with three double bonds need 21.6 kilos, or 289 cubic meters of hydrogen, while a like weight of clupanodonic acid with its four double bonds requires 29 kilos, or 348 cubic meters of hydrogen. The hydrogen requirements per ton of some of the fats enumerated by Sachs are as follows:

	Cubic meters
Cocoanut oil	7.8
Tallow	33.57
Olive oil	68.80
Oleic acid	88.80
Corn oil	143.75

Dr. Holde observes (Seifen. Ztg. (1912), 918) that oleic acid, the most important constituent of all semi-drying liquid oils, requires only 2 parts of hydrogen to 282 parts of oil in order to get stearic acid, while linoleic and linolenic acid require 4 and 6 parts respectively to 280 and 278 parts. Ricinolic acid, which contains one atom of oxygen more than oleic acid, forms an oxystearic acid which has a very high melting point, but which also only contains 2 atoms more of hydrogen than the original acid. The glycerides of stearic or palmitic acid naturally remain unchanged throughout the operation.

† According to Linde (Production of Hydrogen, Third Int. Cong. of Refrigeration, 1913) six to ten cubic meters of hydrogen are required for hardening one hundred kilos of oil.

The following tabulation shows the nature of the reaction in several cases:

$$\left.\begin{array}{ll}\text{Oleic Acid} \ldots\ldots\ldots\ldots\ldots\ldots & C_{18}H_{34}O_2 + 2\,H \\ \text{Linolic Acid} \ldots\ldots\ldots\ldots\ldots & C_{18}H_{32}O_2 + 4\,H \\ \text{Linolenic Acid} \ldots\ldots\ldots\ldots & C_{18}H_{30}O_2 + 6\,H \\ \text{Clupanodonic Acid} \ldots\ldots\ldots & C_{18}H_{28}O_2 + 8\,H \end{array}\right\} = \begin{array}{c} C_{18}H_{36}O_2 \\ \text{Stearic acid} \end{array}$$

$$\underset{\text{Olein}}{(C_{18}H_{33}O_2)_3C_3H_5 + 6\,H} = \underset{\text{Stearin}}{(C_{18}H_{35}O_2)_3C_3H_5}$$

$$\underset{\text{Erucic acid}}{C_{22}H_{42}O_2 + 2\,H} = \underset{\text{Behenic acid}}{C_{22}H_{44}O_2}$$

$$\underset{\text{Ricinoleic acid}}{C_{18}H_{34}O_3 + 2\,H} = \underset{\text{Hydroxystearic acid}}{C_{18}H_{36}O_3}$$

One of the problems in the hydrogenation field is that of a cheap supply of pure hydrogen. The demand for hydrogen in various directions has increased of late and undoubtedly this will lead to improvements in the manufacture of the gas.

The two methods now most favored in the hydrogenation of oils are the iron-sponge steam process and the electrolytic method. For large plants the iron-sponge steam process is preferred, but it is relatively complicated and scarcely to be recommended for plants calling for 1000 cubic feet of hydrogen, or less, per hour.

In the electrolysis of brine to make caustic soda and bleach, there exists a by-product of hydrogen sufficient in amount to treat an enormous quantity of oil. To-day a good portion of this hydrogen is allowed to go to waste. Eventually it may be used, to some extent at least, for hydrogenation purposes. One electrolyic plant in this country is producing about one ton of hydrogen daily. Another plant generates nearly one-half a ton, while a third concern discharges into the air nearly 300,000 cubic feet each day.* In spite of the vast

* Similar conditions exist abroad, Blum reporting (Met. and Chem. Eng. (1911), 157) that enormous amounts of hydrogen gas are produced in the large works for the production of caustic soda and chlorine by electrolysis of common salt solutions. The hydrogen gas is set free together with the caustic soda at the cathode. The quantities are so large, compared with the demand which exists at present for hydrogen, that most of the hydrogen gas is passed unused into the air. The Griesheim-Elektron Company in Germany produces daily 20,000 cubic meters of hydrogen of about 90 to 97 per cent purity. In this case the cost of the gas is practically that of its compression and storage. Special railway cars are built in Germany for the transportation of 500 cylinders containing 2750 cubic meters of hydrogen gas. The cost of shipment of the cylinders is so great that the distribution, of course, is only local, as regards consumption on the large scale. The Zeppelin Garage in Frankfort is supplied with hydrogen by means of a high-pressure main from Griesheim.

amount of by-product hydrogen obtainable, it appears that oil manufacturers prefer to install hydrogen-generating equipment in their present works, rather than to ship oil to a source of waste hydrogen and conduct hardening operations at some relatively remote point.

In consequence the present methods of preparing hydrogen are being carefully scrutinized and new systems for the generation of the gas are being studied and developed. For this reason the whole subject of the production of hydrogen is here reviewed at some length,* the proposed technical methods for its generation being classified as follows:

A. *Water gas as a source of hydrogen.*
   1. Replacement of carbon monoxide by hydrogen.
   2. Liquefaction and other methods for the removal of carbon monoxide.

B. *Decomposition of hydrocarbons.*

C. *Action of steam on heated metals.*

D. *Wet processes and the decomposition of hydrates.*
   1. Action of acids on metals.
   2. Decomposition of water by miscellaneous chemicals.
   3. Electrolysis of water.
   4. By-product hydrogen.

The hydrogen problems involved in the hydrogenation of oils are discussed by **Walter** † who states that a plant for oil hardening cannot well be installed by small concerns, but only by those having powerful financial resources, because the cost of equipping for an adequate supply of hydrogen represents so great an outlay. If water gas or coke oven gas containing 40 to 50 per cent hydrogen could be used the matter would present a different aspect. Water gas contains on the average:

	Per cent
Hydrogen	50
Carbon monoxide	41
Carbon dioxide	4
Nitrogen	4.5
Methane	0.5

A plant for the manufacture of water gas is much cheaper than one for making technically pure hydrogen. Reckoned on the hydrogen content the cost of production of water gas is very much lower than that of pure hydrogen.

* Brahmer, Chemie der Gase, Frankfort, 1911, contains much useful information on the production of hydrogen. The subject of hydrogen production on a commercial scale is treated by Lepsius in Moniteur Scientifique, 1912, 493-500.

† Seifen. Ztg. (1913), 4.

Coke oven gas contains about the following:

	Per cent
Hydrogen	46
Nitrogen	15
Carbon monoxide	7
Methane	20
Ethylene	2
Carbon dioxide	4

This gas may be obtained in large quantities at low cost in the neighborhood of coke oven plants. Many of the patents relating to the hydrogenation of oils refer to the use of gas mixtures containing hydrogen as well as to hydrogen gas in a pure state. These statements, Walter argues, appear apparently only as a precaution in order to preclude others from making application for patent protection on the use of hydrogen-containing gases in the place of pure hydrogen. He regards the investigation of these hydrogen-containing mixtures as never having been properly followed out, but thus far the results obtained are not promising.

Carrying out the hydrogenation process with hydrogen-containing gases involves: (1) the catalyzer must not become contaminated with poisons; (2) the process must proceed in spite of the presence of foreign gases; (3) foreign gases must not injure the oil.

Carbon monoxide and nitrogen in the pure state apparently do not injure the usual catalyzers in the least. As to the remaining impurities the sulfur compounds are catalyzer poisons. It has been noted with water gas that the catalyzer loses its activity much sooner than when pure hydrogen is employed. Foreign gases, which are indifferent in a chemical sense, of course dilute the hydrogen with which they may be mixed, and when one is working with a dilute in place of a concentrated reagent, the action usually is slower. In this connection investigation shows that with increasing dilution of the hydrogen employed, the time required for treatment lengthens, a result which, of course, ordinary practice would indicate is to be expected. Also hardening cannot easily be carried as far with hydrogen-containing gases as with pure hydrogen. It can be stated as a general rule that in oil hardening the hydrogen conducted into the oil is not wholly absorbed, but goes as a stream of gas through or in contact with the oil, so a considerable proportion of the hydrogen introduced is not used. When one is using water gas in place of hydrogen, the former gives up only a portion of its hydrogen to the oil. The hydrogen available to the oil is thus proportionately less than with ordinary hydrogen gas, and repeated conveyance of the partially-used water gas through the oil is as good as useless because of the great reduction in the proportion of hydrogen.

Since only a part of the hydrogen contained in water gas may be utilized, it is necessary to employ relatively a much larger quantity of the latter. Of the 50 per cent or so of hydrogen contained in

water gas, according to Walter, only about one-third or approximately 17 per cent of the total gas is used. To secure the same effect 600 cubic feet of water gas in place of 100 cubic feet of hydrogen are required, in which case about 500 cubic feet of spent gas results. The spent gas, of course, should not be thrown away as this would be wasteful and arrangements must be made for its use in heating, lighting or power applications. It is not always convenient to thus make use of such a large volume of hydrogen-spent gas; furthermore it is necessary to make all the pipes and connections larger by six-fold than when concentrated hydrogen is employed, which means an additional expense.

Finally there is the question as to whether or not the foreign gases * contained in water gas exert any detrimental influence upon the hardened oil; whether they do not during the process bring about side reactions. As regards carbon monoxide † and carbon dioxide no chemical action on oils or fatty acids under these conditions is known, yet eventually catalyzers may be employed which cause side reactions. If the hardened oil is to be used for technical purposes such reactions probably need not be feared, but for edible purposes this may not obtain. In this connection Bomer has laid down the condition in oil hardening that the hydrogen employed must be pure when the fat is to be used for edible purposes. Thus when using water gas in place of hydrogen, a number of difficulties are likely to arise in large scale operation and the seeming financial advantage on close inspection shrinks considerably, practically leaving the field to technically pure hydrogen.‡

* The addition of small quantities of a second gas to a pure gas markedly reduces the rate of diffusion in liquids, according to Barus (Chem. Abs. (1913), 3871).

† Caro (Seifen. Ztg. (1913), 852) considers the presence of carbon monoxide in hydrogen used for hardening fats with nickel catalyzers to be, under some circumstances, injurious to the catalyzer. Maintaining the temperature of the oil during hydrogenation above 200° C. is said to be beneficial, as any nickel carbonyl formed will be at once decomposed at that temperature.

‡ The importance of the problem of securing hydrogen in large quantities is evidenced by an order recently placed by an American oil concern for 2 gasometers to hold hydrogen, each said to have a capacity of about 1,000,000 cubic feet of the gas.

Goldschmidt (Seifenfabr., 32, 713) states that a good and cheap source of hydrogen gas is one of the greatest problems connected with the process; that such impurities in the gas as arsenic, phosphorus, hydrogen sulfide, mineral acids, carbon bisulfide, chloroform and acetone poison catalysts of the platinum group; while sulfur, chlorine, bromine and iodine unfavorably affect those of the nickel group.

Fry states that negative hydrogen has been shown to act as a reducing agent, since it naturally tends to revert to its ordinary state, positive hydrogen, which change is accompanied by the liberation of electrons. (J. S. C. I., 1914, 271.)

CHAPTER XIII

WATER GAS AS A SOURCE OF HYDROGEN AND THE REPLACEMENT OF CARBON MONOXIDE BY HYDROGEN

Many suggestions have arisen for the production of hydrogen from water gas, involving replacement of the carbon monoxide present by hydrogen through the reaction

$$CO + H_2O = CO_2 + H_2.$$

Because of the incompleteness of the reaction, those methods proposed which do not take cognizance of the accumulation of carbon dioxide and consequent repression of the progress of the reaction have not been particularly successful. The reaction is a reversible one and unless means are taken to remove the carbon dioxide as formed, the resulting gas mixture contains hydrogen, carbon dioxide and carbon monoxide usually in such proportion as to be too costly of purification for handling on the large scale. In consequence lime or other alkali has been suggested for absorbing the carbon dioxide. These suggestions appear in the patents to Tessie Du Motay and the Chemischen Fabrik Greisheim-Elektron, as will be pointed out in a more detailed manner in the following.

Engels * has made a careful study of the reaction between carbon monoxide, water vapor and lime. The investigations show that the most suitable temperature lies between 450° to 550° C. Below 450° C. the reaction progresses too slowly, while above 550° C. the conversion does not go to completion or side reactions occur. Engels studied the effect of additions of an oxide, such as iron oxide, to the lime in order to catalytically hasten the reaction and found its course to be much improved by the addition of a few per cent of such catalyzer. The reaction is exothermic so no further external heating is necessary after the conversion has begun.

In 1880 **Tessie du Motay** devised a process for the production of hydrogen from water gas.† The latter gas mixed with steam is

* Über die Wasserstoffgewinnung aus Kohlenoxyd und Kalkhydrat, Dissertation, Karlsruhe, 1911.

† U. S. Patents 229,338, 229,339 and 229,340, June 29, 1880.

passed into a converter containing lime where hydrogen and calcium carbonate are formed. Fig. 57 shows a plan view of the apparatus, in which *A* is a water-gas generator, *B* represents purifiers in which

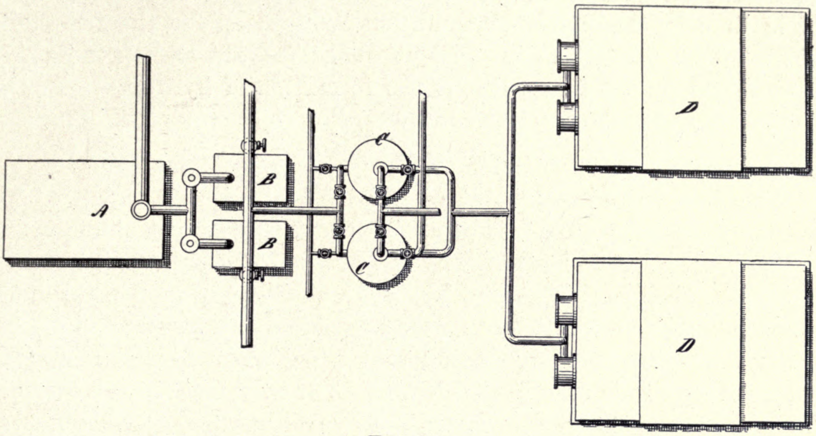


FIG. 57.

sulfur is removed, *C* designates superheaters where steam is mixed with the water gas. The preheated mixture then passes to a converter shown in Fig. 58. The inclined passageways of the latter are filled with lime in contact with which the reaction

$$CO + H_2O = CO_2 + H_2$$
$$CO_2 + CaO = CaCO_3,$$

progresses, yielding hydrogen gas. In lieu of water gas, coal gas or the vapor of naphtha may be similarly treated.

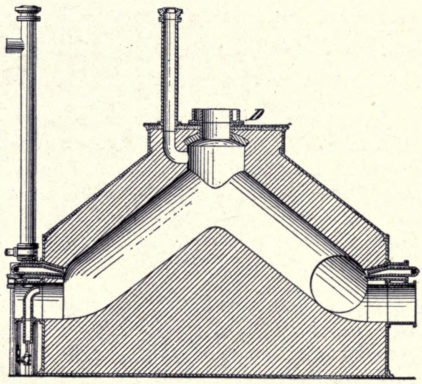


FIG. 58.

The process of the **Chem. Fabrik Greisheim-Elektron,** referred to above,* involves mixing water gas with an excess of steam and passing this mixture over lime or hydrated lime to which about 5 per cent of iron powder has been added. The lime is heated to approximately 500° C. in an upright retort fitted with an agitator. The following reaction takes place:

$$Ca(OH)_2 + CO = CaCO_3 + H_2,$$

* Zeitsch. f. angew. Chem. (1912), 2401; British Patent 2523, Feb. 2, 1909.

with evolution of heat, and the reaction chamber is cooled so that the temperature does not exceed 500° C., or the temperature at which calcium carbonate commences to dissociate. The carbonate is regenerated by subsequent calcination.* The presence of water vapor or of lime in the hydrated condition is essential for the reaction.† If absent or present in insufficient quantities the carbon monoxide is absorbed by the lime without the formation of hydrogen. In the absence of water the reaction runs according to the following equation:

$$CaO + 2\,CO = CaCO_3 + C.$$

According to the statement of Lepsius hydrogen of 97.5 per cent purity is obtained at a cost of about 2 to 2.5 cents per cubic meter.

The production of hydrogen by the action of carbon monoxide and steam on quicklime is regarded by **Levi** and **Piva** ‡ to be dependent on the intermediate formation of calcium formate.

Merz and **Weith** § have noted that when moist carbon monoxide is passed over soda lime heated to 300° C. or over, hydrogen is formed. A simple process for the production of hydrogen based on the observations of Merz and Weith has been put forward by the **Société générale des Nitrures in Paris.** A mixture of producer gas and water gas is treated in the usual way to remove carbon dioxide and is then passed over hot lime, which treatment yields a mixture of nitrogen and hydrogen free from carbon monoxide. The composition of the hydrogen-nitrogen mixture may be adjusted by using different proportions of the producer gas and water gas.‖

Jerzmanowski ¶ makes a hydrogen-containing gas with apparatus shown in Fig. 59. A kiln *B* filled with lime is raised to a high temperature by burning producer gas from the generator *A*. As soon as a sufficient heat is attained in *B*, an injector *H* blows into *B* steam and petroleum, which are decomposed chiefly into hydrogen and carbonic acid along with small quantities of carbonic oxide, marsh gas and other impurities. The gases pass through a cooler *C* to the gasometer *D*, and thence to purifiers.**

* The Chemische Fabrik Griesheim-Elektron (British Patent 13,049, June 3, 1912) mix steam with gas containing carbon monoxide and pass the mixture upwards through towers packed with pieces of lime and heated to between 400° and 700° C. The lime, when exhausted owing to conversion into calcium carbonate, can be regenerated in situ by diverting the stream of gases and recalcining.

† U. S. Patent 989,955, April 18, 1911, to Ellenberger, assigned to the Chemische Fabrik Griesheim-Elektron, discusses these reactions.

‡ J. S. C. I., 1914, 310.

§ Ber. (1880), 719. See also Ber. 1880, 31.

‖ Sander, Zeitsch f. angew. Chemie (1912), 2406.

¶ J. S. C. I., 1884, 560.

** The New York Oxygen Company produce hydrogen by heating together anthracite and slaked lime. On passing an excess of steam over the residue in the retorts the reverse action sets in and the slaked lime is reproduced. This sequence may be continued many times without renewing the materials. (J. S. C. I., 1887, 92.)

By another process steam is allowed to act on carbon or carbonaceous matter to which both an alkali compound and lime have been added, the effect of the additions according to Dieffenbach and Moldenhauer (British Patent 8734, April 11, 1910) being to lower the temperature of decomposition and to give hydrogen free from compounds of carbon and oxygen. For example, 100 kilos of charcoal or coke, impregnated with a 10 per cent solution of potassium carbonate, are mixed with 500 kilos of quicklime, and the mixture is decomposed by steam at 550° to 750° C.

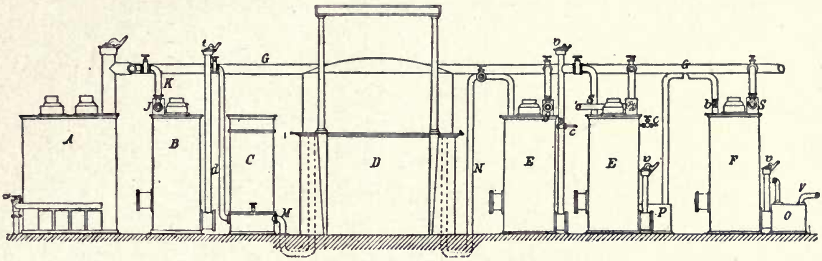


FIG. 59.

They also claim (British Patent 7718, March 30, 1910) the employment of other alkali compounds — such as chlorides and sulfates — for the same purpose. The fuel is impregnated with a solution of the alkali compound and dried, or, if practical, the fuel is coked after the addition of such compound. A comparatively small amount of oxygen may be introduced along with the steam for the purpose of maintaining the required temperature inside the decomposition apparatus. Granulated coal or coke may be treated with a solution of an alkali silicate or carbonate and the mixture briquetted and subjected to the action of superheated steam at temperatures from 550° to 750° C.*

Hembert and **Henry** † pass superheated steam in a fine spray over coke heated to redness, whereby a mixture of hydrogen and carbon monoxide is formed. This mixture is led into a second retort filled with fireproof materials, also heated to redness. In the second retort steam is allowed to enter heated to its point of dissociation. These gases act upon one another, hydrogen and carbon dioxide being formed. The carbon dioxide may be absorbed by milk of lime. In this way 3200 cubic meters hydrogen are said to be obtained from 1 ton of coke.

In the production of a mixture of hydrogen and carbon dioxide by the action of steam on carbonaceous substances or on water gas, Sauer (German Patent 224,862, May 9, 1907) proposes to use an excess of steam and to superheat this to such a degree that it suffices to maintain the proper reaction temperature, in order to ensure the production of a gas of uniform composition. For example in the action of steam on coal, the latter is not blown alternately with air and steam, but the

* French Patent 417,929, April 25, 1910.
† Compt. Rend. (1885), 101, 797.

steam is superheated to such a degree that when the process is once started it is supposedly carried on continuously by aid of the heat of the steam alone.*

For treating hydrogen and carbon compounds to oxidize the carbon to carbonic acid, in which form it may be readily eliminated, leaving pure hydrogen, **Moore** † brings the hydrogen and carbon compounds in a suitably divided state (generally as a gas or fine spray) into contact with heated oxide of iron, manganese, copper, tin, lead or zinc, in the presence of a jet of superheated steam. During the operation the oxides are said to be alternately reduced and reoxidized, acting as carriers of oxygen between the steam and the carbon compounds, so that the carbon present is converted into carbon dioxide, and leaves the chamber in which this is effected mixed with the hydrogen originally present and that resulting from the decomposition of the steam. The carbon dioxide may be removed by any known method, such as absorption by lime, or by water under pressure, or by a solution of alkaline carbonate.

Mond and **Langer** (British Patent 12,608, Sept. 1, 1888) bring carbonic oxide or gaseous hydrocarbons into contact with metallic nickel at a temperature of 350° to 400° C., or with metallic cobalt at 400° to 450° C., when decomposition takes place into carbon and carbonic acid or hydrogen, the carbon combining with the metal. If now steam, at a moderate temperature, be introduced this carbon combines with oxygen to produce carbonic acid, with simultaneous formation of free hydrogen. These various reactions take place simultaneously when the steam is passed through the apparatus along with the carbonic oxide or hydrocarbon, the ultimate products being carbonic acid and hydrogen. The former can be eliminated by any suitable means, such as by washing with milk of lime. The cobalt or nickel surfaces may be obtained by impregnating pumice stone with a solution of the metal, and reducing.

Similarly **Elworthy** ‡ heats a mixture of water gas and steam in the presence of such metals as nickel or iron to a sufficiently high temperature to induce the reaction,

$$CO + H_2O = CO_2 + H_2,$$

whereby the hydrogen originally present in the water gas is increased by a volume equal to that of the carbon monoxide contained in it. The resulting carbon dioxide is removed by absorption by water under pressure, or by alkalis, or by other known means.

Ellis and **Eldred** § generate a hydrogen-containing gas as follows:

* Green (British Patent 13,510, July 13, 1895) states he obtains hydrogen from water by an improved process, "which consists in burning steam with hydrogen gas, or with carburetted hydrogen, or carbon monoxide within a suitable chamber."

† J. S. C. I., 1885, 450.

‡ French Patent 355,324, June 17, 1905.

§ U. S. Patent 854,157, May 21, 1907.

Producer gas, generated by blowing air through a producer charged with fuel, is led through a superheating chamber filled with checker-work of refractory material. The gas is then passed under a boiler and burned to generate steam. Water gas is mixed with steam and passed through the superheater to convert the carbon monoxide into dioxide. The mixture of carbon dioxide and hydrogen is then compressed; the former is separated in the liquid condition and the latter is collected separately. The process is rendered continuous by repeating the above steps alternately.*

The essential feature of a process devised by **Dieffenbach** and **Moldenhauer** † is that a mixture of steam with a hydrocarbon or other suitable organic compound is heated to the temperature of reaction, or kept in contact with a catalytic body for only a short time and is then suddenly cooled or removed from the catalyzer, in order that the carbon dioxide formed shall have little or no opportunity for being reduced to carbon monoxide. From the resulting mixture of hydrogen and carbon dioxide, the latter can easily be removed, leaving more or less pure hydrogen. A suitable way of carrying out the process is to use as catalyzer wire gauze of nickel, cobalt, platinum, etc., disposed transversely to the direction of flow of the gases, and heated electrically to the requisite temperature. Instead of using external heating, the required temperature may be attained partly or entirely by combustion of a portion of the hydrocarbon by means of admixed oxygen.

Naher and **Muller** ‡ prepare water gas by blowing superheated steam into a generator filled with coke, which has been heated to about 1000° C., and exhausted, and the gas produced, mixed with superheated steam, is passed over a contact mass of rhodium- or palladium-asbestos at 800° C. The resulting hydrogen then is freed from the accompanying carbon dioxide.

Carbon monoxide and steam are caused to interact at 300° to 600° C. under a pressure of 4 to 40 atmospheres in the presence of a catalyst, such as iron, nickel, or the like, with the production of carbon dioxide and hydrogen, the former being removed by absorption according to a process devised by the Badische Company.§

In order to better effect the reaction betweeen carbon monoxide and water vapor in the presence of heated catalytic material and to carry on the operation continuously the **Badische Company** inject

* Ellis and Eldred employ nickel, iron or manganese as catalytic material.

† German Patent 229,406, June 3, 1909.

‡ German Patent 237,283, Sept. 30, 1910.

§ British Patent 26,770, Nov. 21, 1912.

oxygen or air into the reaction chamber thus securing the necessary heating effect.*

Pullman and **Elworthy** † generate a mixture of hydrogen and carbon dioxide by passing superheated steam in excess over red-hot coke or charcoal contained in a cast-iron retort, and the mixed gases after cooling are led through a number of porous pipes made of plaster of Paris or unglazed earthenware where they are separated to a great extent by diffusion, the hydrogen passing more rapidly through the porous walls of the pipes than the carbon dioxide.

After leaving the diffusing apparatus the nearly pure hydrogen is compressed into suitable vessels partially filled with water to absorb most of the remaining carbon dioxide. On opening the valves of the vessels the hydrogen rapidly escapes, and may be collected in a suitable holder and then given a final purification, either by washing with water in a scrubber or by passing it over some absorbent for carbonic acid, such as damp hydrate of lime, or through milk of lime. Instead of separating the mixed gases by diffusion, they may be taken from the cooling apparatus direct and compressed in strong metal vessels partially filled with water. The carbonic acid being much the more soluble, on opening the vessels hydrogen at first escapes rapidly and may be collected, the carbonic acid being afterwards collected in a separate receiver. The gases may be submitted to this operation several times over, and finally purified as above. Or instead of using water, glycerine or hydrocarbon oils which absorb more gas and part with it more slowly may be used.

That complete replacement of carbon monoxide by hydrogen in processes involving heating water gas and steam is impossible because of the conditions of equilibrium which obtain, is discussed by **Gautier** (Bull. Soc. Chim. (1906), **35**, 929) who refers to the work of Boudouard (Bull. Soc. Chim. (1901), **25**, 484). The latter determined the ratio $\frac{CO}{CO_2}$, in the equilibrium between carbon monoxide, steam, carbon dioxide, and hydrogen at different temperatures; and Hahn (Z. Physik Chem. (1903), **42**, 705; **44**, 513; (1904), **48**, 735) determined the coefficient $K = \frac{CO \times H_2O}{CO_2 \times H_2}$, at different temperatures. When a current of carbon monoxide mixed with a varying excess of steam is passed through a porcelain tube heated to 1200° to 1250° C., at the rate of about 1 liter of the mixed gases per hour, or when a dry mixture of equal volumes of carbon dioxide and hydrogen is similarly treated at 1300 degrees, the reaction proceeds until the volume of hydrogen is about double that of carbon monoxide. The reactions correspond with the equations:

$$3\,CO + 3\,H_2O = CO + H_2O + 2\,H_2 + 2\,CO_2,$$
$$3\,CO_2 + 3\,H_2 = CO + H_2O + 2\,H_2 + 2\,CO_2.$$

Under these conditions, any mixture of carbon monoxide, steam, hydrogen and carbon dioxide tends towards the composition, $CO + H_2O + 2\,H_2 + 2\,CO_2$. Small quantities of formic acid, but no formaldehyde, are produced.

Additional matter by Gautier appears in Comptes rendus (1910), **150**, 1564, considering the reaction particularly from the reverse standpoint, that is, the reduc-

* British Patent 27,117, Nov. 25, 1912; Chem. Zeit. Rep. (1913), 696.
† British Patent 22,340, Dec. 21, 1891.

tion of carbon monoxide by hydrogen. The results show that by heating carbon monoxide in the presence of hydrogen, water is actually formed. The reduction begins approximately at 200° C. The maximum formation of water is between 1100° and 1200° C.*

By a process of the **Badische Company** † water gas is passed with an excess of steam over heated finely-divided metals of the iron group, especially iron, cobalt and nickel, or their oxides, and the carbon dioxide formed is eliminated from the gaseous reaction product. The catalyst is best prepared by the addition of appropriate diluents or binding agents, organic or inorganic, which may be such as to give off gas on heating so as to increase the porosity. For example, dry precipitated ferrous carbonate may be made into a plastic mass with lime, water, potassium hydroxide and ferric nitrate, and the mixture dried and heated to 500° C. A reaction temperature of preferably not over 600° C. is maintained by adjusting the temperature of the gases before they enter the contact chamber.

* Met. and Chem. Eng. (1911), 511.
† French Patent 459,918, July 2, 1913.

CHAPTER XIV

LIQUEFACTION AND OTHER METHODS FOR THE REMOVAL OF CARBON MONOXIDE

As uncarburetted or blue water gas consists of approximately equal parts hydrogen and carbon monoxide with small amounts of other gases, much attention has been given to methods of eliminating the monoxide by solution, absorption and liquefaction. The cost of removal of the carbon monoxide by solvents such as cuprous chloride and the like appears to be too great for commercial application. As the monoxide is relatively easily liquefied by cold and pressure, while hydrogen is extremely resistant to liquefaction under like conditions, processes have been devised for removing carbon monoxide in this way. As a source of cheap hydrogen this method offers attractive possibilities to concerns requiring large amounts of the gas. For small plants the relatively high cost of installation renders the use of liquefaction processes less feasible.

The pioneer work connected with the development of the liquefaction system towards a commercial goal should be credited to C. E. Tripler, who apparently was the first to devise methods and apparatus for large scale liquefaction of air and other gases. In 1893 Tripler patented * the method of condensation "of a current of gas by expansion of itself over the conduit through which it passes." On this idea is based the present systems of separating hydrogen and carbon monoxide through liquefaction of the latter.

The principle of liquefaction by compression with counter-current cooling is shown diagrammatically in Fig. 60. The reducing valve *R* is so arranged that on the side carrying the receiver *B* for the liquefied product a pressure of 20 atmospheres is maintained, while on the other side the pressure is held at 200 atmospheres. The operation is as follows. Air is drawn from *B* by the compressor *K*, passing through the outer concentric tube of the coil. After compression to 200 atmospheres the air enters the cooler *KG* where the heat generated by compression is absorbed. The cooled compressed air flows through the inner tube of the coil to the reducing valve *R* where it is released

* British Patent 4210, 1893.

at 20 atmospheres. Circulation in this manner is kept up until the temperature is lowered to the point of liquefaction.

Nitrogen boils at − 193 degrees, carbon monoxide at − 190 degrees and carbon dioxide at − 78 degrees while hydrogen boils at − 252 degrees and may easily be retained in gaseous form at temperatures which convert the other components of water gas to liquids or solids.*

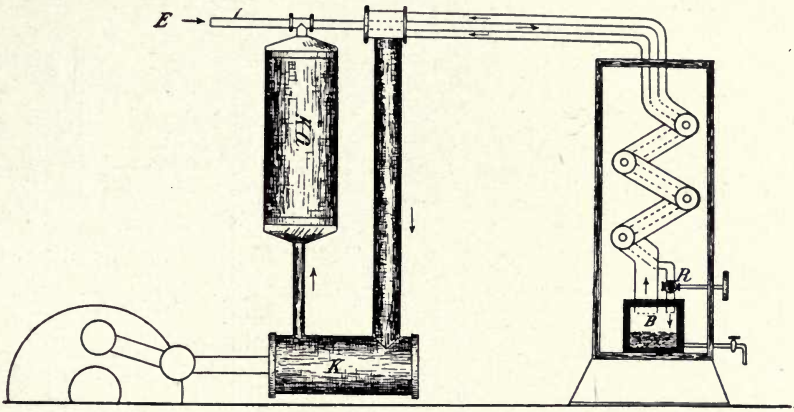


FIG. 60.

Apparatus in various forms has been devised by Linde,† Claude, Hildebrandt and others for the separation of the components of mixed gases by the liquefaction of the more easily liquefied constituents. The **Hildebrandt** system, shown in Fig. 61, consists of a coil of pipe of relatively large diameter through which two smaller pipes extend. The latter are indicated by 1 and 7 in the upper right-hand terminus of the large coil. Gas under the requisite high pressure enters at 1, passes along one of the small pipes within the larger pipe of the large coil, emerges at 2 and passes along the central riser to the expansion chamber *E*. Expansion with liquefaction occurs here. The liquefied product flows through 3 into the chamber *R* and from thence into a multiple evaporating coil 4, which consists of four coiled pipes having openings along their upper sides. Evaporation of the more easily boiling constituents takes place as the product flows downwardly along the evaporating conduits. The vaporized portion departs through the perforations of the coil and passes through 5 into the large pipe *A*, moving along this pipe as a current counter to the high-pressure gas entering at 1 and passing out of the system by the horizontal pipe shown on the upper right hand. The liquid fraction collecting in *G* flows along one of the narrow pipes to 2, thence through one of the narrow pipes in the large coil, upwardly and out at 7.

* The production of hydrogen by liquefaction is clearly described by Linde in the Proceedings of the Third Int. Congress of Refrigeration, 1913. See also a very comprehensive treatise entitled, "Lowest Temperatures in Industry," issued by Gesellschaft für Lindes Eismaschinen, Munich.

† In a publication entitled "Lowest Temperatures in Industry," it is stated that five plants have been supplied by the Linde Co. for fat-hardening purposes and that

Linde makes note * that **Frank** and **Caro,** with the aid of the Linde firm, have succeeded in the production of hydrogen of a high degree of purity from water gas. Figs. 62 and 63 show the apparatus diagrammatically.

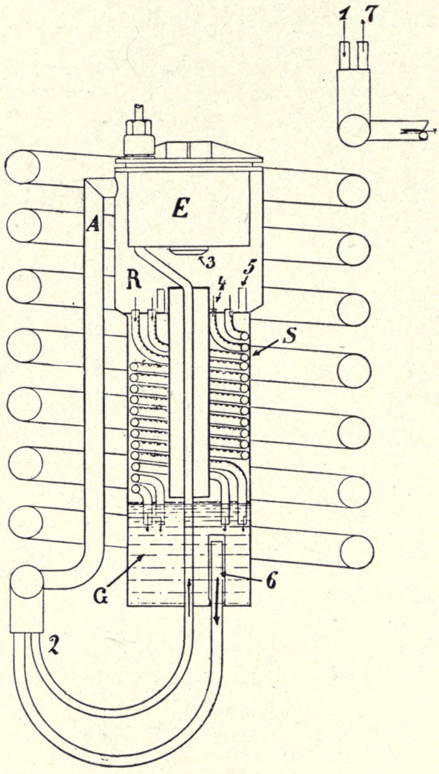


FIG. 61.

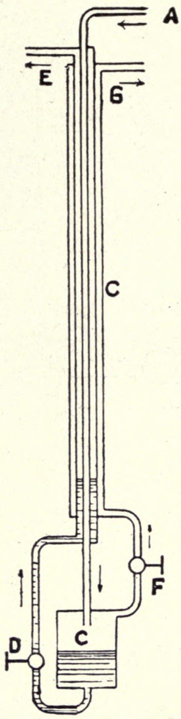


FIG. 62.

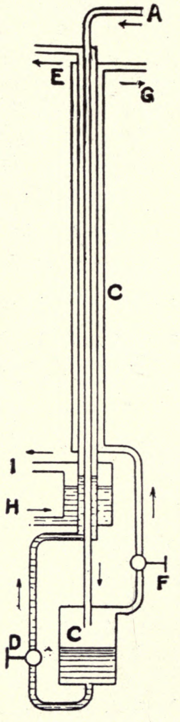


FIG. 63.

Compressed water gas enters by the innermost tube *A*, and is cooled by expansion through the valves and return of the cooled gases by the middle and outermost tubes *G* and *E* respectively, until liquefaction of the carbon monoxide occurs; separation then takes place, the gaseous hydrogen escaping through the valve *F* and the tube *G*, the liquid carbon monoxide passing through the valve *D* and evaporating

the total capacity of these is over 1000 cubic meters per hour. A plant in St. Petersburg uses 100 cubic meters; another in Nishnj-Nowgorod 30 cubic meters; Bremen-Bersigheimer Ölfabriken 200 cubic meters; United Soap Works, Ltd., Rotterdam, 200 cubic meters; and Ardol Co., Leeds, 500 cubic meters per hour.

* J. S. C. I., 1911, 746.

in the middle tube. It was found impossible to liquefy the carbon monoxide, however, by the small amount of cooling by internal work of a gas containing so much hydrogen, and the cooling was therefore aided, as indicated in Fig. 63, by cold-jacketing the lower portion of the apparatus by means of a similar apparatus producing liquid air; in this way the industrial success of the apparatus was secured, and a gas produced, containing hydrogen, 97 per cent; carbon monoxide, 2 per cent; nitrogen, 1 per cent. Removal of the carbon monoxide by calcium carbide or soda lime then yields a 99 per cent hydrogen. The gas formed from the liquid contains 85 to 90 per cent of carbon monoxide, the rest being chiefly hydrogen, and is an excellent power gas.

By one process (Ges. für Linde's Eismaschinen A. G., French Patent 427,983, March 31, 1911) the strongly-cooled, compressed gaseous mixture containing hydrogen is passed through a heat interchanger so as to separate it into a gaseous portion, chiefly hydrogen, and a liquid portion, consisting mainly of impurities. The mixture passes into a receiver, which is provided with two separate systems for producing expansion; the liquid portion of the mixture collects in the receiver and is expanded in the lower system, from which it passes into the interchanger in the space surrounding the tube which conveys the original mixture into the receiver, and in the opposite direction to that of the gaseous current; the gaseous portion is expanded in the upper system and passed into the interchanger in the space surrounding the tube which conveys the mixture expanding from the lower system. From the interchanger the expanded hydrogen is collected free from impurities, which are thus condensed by the cold produced by the agency of the above-mentioned expansions. A supplementary refrigerating appliance, containing liquid air or liquid nitrogen, is used in conjunction with the apparatus for the preliminary cooling of the gaseous mixture.

A modified form of the foregoing consists in removing the portion of the gaseous mixture which is not liquefied, and comprises chiefly hydrogen, without allowing it to expand, the pressure remaining equal to that to which the compressed gaseous mixture has been brought. Liquid air or liquid nitrogen, used for refrigeration, is evaporated at a pressure below that of the atmosphere, in order to obtain a more complete separation of the remaining impurities. The liquid air or liquid nitrogen is thus used only for the ultimate refrigeration of the hydrogen which has already been freed from the main quantity of condensable gases. Also, the hydrogen, before it is brought to the expansion apparatus may be subjected to slight heating in a countercurrent device, by means of the compressed gaseous mixture which has not yet been fractionated.*

Frank † cools water gas in a suitable apparatus sufficiently to liquefy the carbon monoxide and dioxide, which are then separated. If the water gas has been produced at a low temperature, and contains

* Ges. für Linde's Eismaschinen A. G., First Addition, to French Patent 427,983, March 31, 1911. See also U. S. Patents to Carl von Linde 1,020,102 and 1,020,103, March 12, 1912; 1,027,862 and 1,027,863, May 28, 1912; 727,650 and 728,173, May 12, 1903.

† British Patent 26,928, Nov. 27, 1906.

chiefly carbon dioxide, with but little carbon monoxide besides hydrogen, it may be completely liquefied, and the hydrogen recovered by fractional distillation. In either case the hydrogen resulting is further purified by being conducted over calcium carbide at a temperature of over 300° C.*

The arrangement of a plant under the **Linde-Frank-Caro** system † is shown in Fig. 64. In this illustration *a* is a water-gas generator to

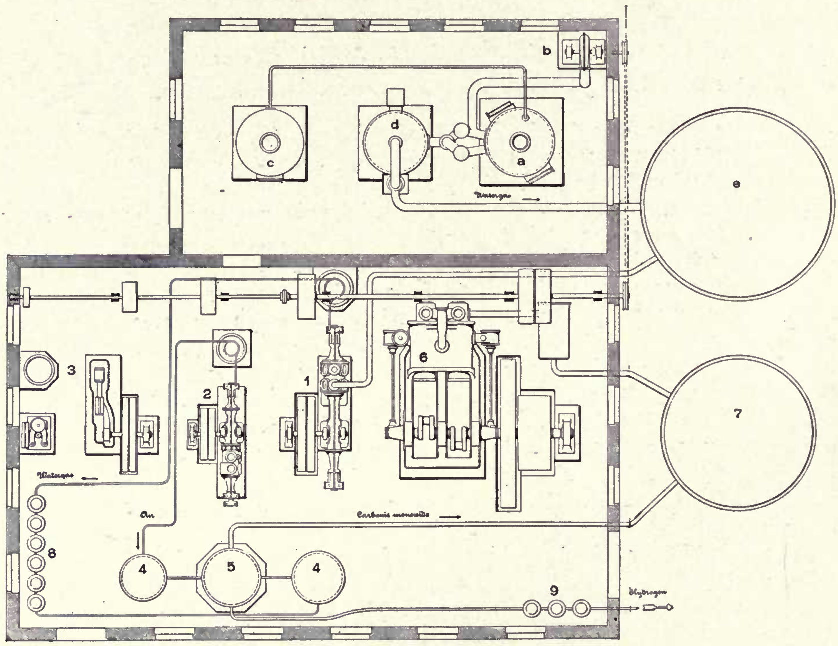


Fig. 64.

which air from the blower *b* and steam from the boiler *c* is alternately supplied. *d* is a scrubber and *e* a gasometer. 1 is a water-gas compressor, 2 an air compressor and 3 a refrigerating apparatus. Fore-coolers for drying the air and water gas are shown at 4. A water-gas separator indicated by 5 is also used for the liquefaction of air. A gas engine 6 operated by the rejected carbon monoxide (collected in gasometer 7) furnishes power for running the compressors. 8 represents

* Frank (J. Gasbeleucht, June 10, 1911) has recommended (see J. S. C. I., 1911, 746) that apparatus for the production of pure hydrogen and other gases by cooling and liquefaction should be installed at gas works making water gas to enable hydrogen to be supplied on the large scale.

† Gesellschaft für Lindes Eismaschinen.

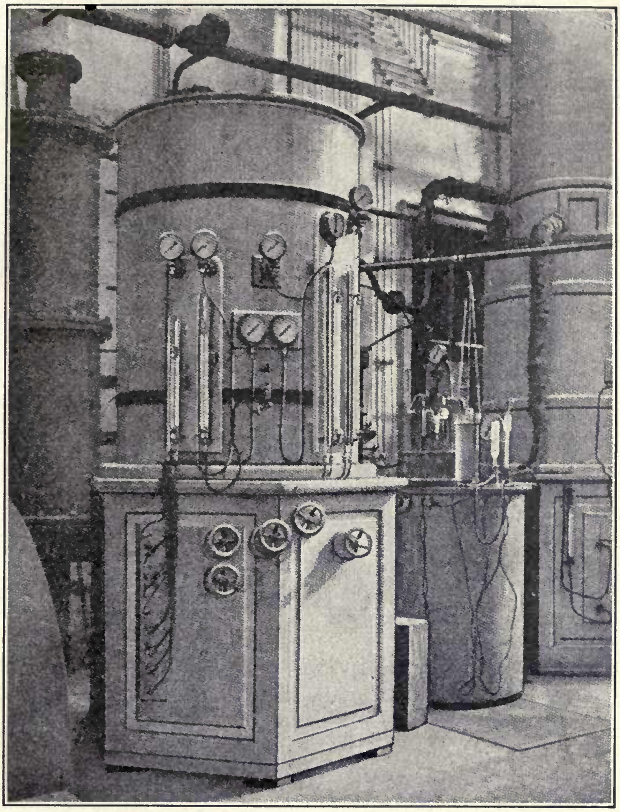


Fig. 65. Linde hydrogen apparatus.

purifiers for removal of carbon dioxide * and 9 soda-lime purifiers for the ultimate purification of the hydrogen. Before purification by soda lime the gas consists of

	Per cent
Hydrogen	97–97.5
Carbon monoxide	1.7–2
Nitrogen	1.0–1.8

and after such treatment the composition is:

	Per Cent
Hydrogen	99.2–99.4
Nitrogen	0.6– 0.8

An apparatus for separating hydrogen from the other constituents of water gas is shown in Fig. 66.†

* The Bedford method of removing carbon dioxide by washing the gas under high pressure, with water, is used.

† Maschinenbau-Anstalt Humboldt, French Patent 445,883, July 8, 1912.

Water gas is compressed until the carbon monoxide is liquefied, impurities such as carbon dioxide are removed in the usual manner, and the mixture of hydrogen and carbon monoxide is introduced into a separator *a*, from which it passes through a concentric tube system *b*, in counter-current to the separated cold gases, to a worm *c*, situated in an evaporator *d*, which is partly filled with liquid carbon monoxide. The mixture expands by way of the valved injector *e*, into a condenser *h*, at the bottom of which the liquid carbon monoxide accumulates, while gaseous hydrogen ascends into a riser *i*. Here the entrained carbon monoxide vapor settles by virtue of its greater density, allowing pure hydrogen to pass by way of an overflow-pipe *k* into the concentric tube system *b* and out of the separator at *l*. The liquid carbon monoxide, which accumulates in *h*, passes through an overflow-pipe *m*, controlled by a regulator *o*, down along the chamber *n*, into the evaporator *d*, leaving in the upper part of *n* any accompanying hydrogen, which may be withdrawn. The liquid carbon monoxide, which accumulates at the bottom of *d*, is evaporated by the worm *c*, and the gaseous carbon monoxide escapes by way of the pipe *p*, through the tubular system *b*, and out of the apparatus at *l*. By making the riser *i*, and chamber *n*, of the requisite height, the two gases may be obtained of the required degree of purity.

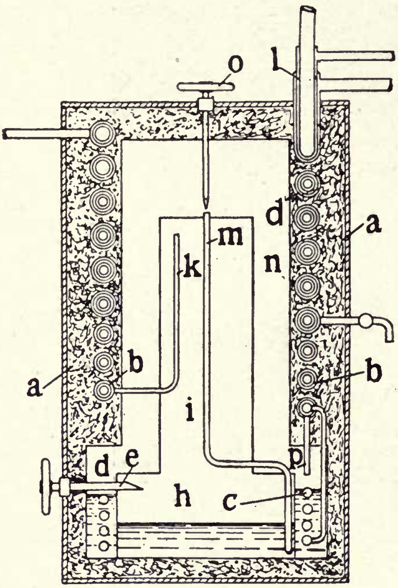


Fig. 66.

A process for the separation of hydrogen from carbon dioxide has been proposed by **Claude.*** The hydrogen containing carbon dioxide is subjected to a pressure of, say, 30 atmospheres, and is then passed through heat-exchangers wherein it meets cold gas passing in an opposite direction. The temperature of the gaseous mixture falls progressively, and the carbon dioxide gradually liquefies. The temperature should not be low enough for the production of solid carbon dioxide. The counter-current of cold gas may be the non-liquefied portion of the compressed gaseous mixture, the cold end of the heat-exchanger being cooled externally by suitable means. Claude † partially liquefies water gas or analogous gaseous mixture so as to give pure hydrogen and carbon monoxide containing hydrogen in solution, and the latter mixture is submitted to the action of heated slaked lime or other

* French Patent 375,991, May 28, 1906.
† French Patent 453,187, March 28, 1912.

material capable of reacting to yield more or less pure hydrogen which is added to the water gas about to be treated.*

Elworthy † separates carbon dioxide from a mixture of gases derived from water gas, containing hydrogen, carbon monoxide, methane, and carbon dioxide by simple compression of the cooled gaseous mixture, or by compression followed by expansion, when the carbon dioxide is liquefied or solidified, and can be removed. The gases escaping from the apparatus are utilized for cooling the incoming gases.

Jouve and **Gautier** ‡ propose to pass water gas through a porous partition, such as unglazed porcelain, in order to separate hydrogen by reason of its rapid power of diffusion. It is said that by one such operation the percentage of carbon monoxide may be reduced from 45 to 8 per cent.

According to **Elsworthy** § water gas may be passed through a centrifugal gas separator, which is said to remove the bulk of the hydrogen, almost free from other gases.

Separation of hydrogen by an absorption method is recommended by **Vignon.** ‖ Water gas, cooled and washed, is treated in a scrubber with an acid or alkaline solution of cuprous chloride, thus absorbing carbon monoxide; the hydrogen is thereby obtained free from carbon monoxide. The latter gas is recovered by heating the solution or subjecting it to reduced pressure, and the cuprous chloride is then used again. The carbon monoxide may be utilized by mixing it with air and burning it in the water-gas generator, so as to supply the heat necessary for the formation of the water gas, or this may be effected by burning the monoxide in a vertical shaft, filled with refractory material, fixed in the center of the generator.

Frank ¶ passes dry water gas over calcium carbide at a temperature above 300° C. Carbon monoxide reacts with the carbide forming calcium oxide, calcium carbonate and carbon, while the nitrogen present is converted into calcium cyanamide.**

* The Claude Company (Chem. Ztg. Rep. (1913), 521; French Patent 453,187, March 28, 1912) indicate that the present attainable yield (about 50 per cent) of hydrogen by the liquefaction system is increased and the loss through solution of hydrogen in carbon monoxide is diminished if the carbon monoxide gas carrying hydrogen is subjected to the action of hydrated lime to form calcium carbonate and hydrogen and the impure hydrogen thus secured is mixed with water gas and further treated in a similar manner.

† First Addition, June 16, 1906, to French Patent 355,324, June 17, 1905.

‡ French Patent 372,045, 1906.

§ British Patent 10,581, May 5, 1906.

‖ French Patent 389,671, April 27, 1908.

¶ French Patent 371,814, 1906.

** Thorpe Dict. App. Chem. III., 61.

Frank conducts water gas through milk of lime to remove carbon dioxide, then through cuprous chloride in hydrochloric acid solution to remove carbon monoxide and over heated calcium carbide to remove nitrogen as cyanamide. The carbide also removes traces of carbon monoxide and dioxide with separation of carbon in a finely-divided condition. The cuprous chloride solution is regenerated by exposing to reduced pressure to remove the monoxide.* Subsequently Frank stated † that the expense of carbide, or of cuprous compounds or other means of absorbing carbon monoxide, was found to be too great and ultimately he was led to adopt the method of removal by liquefaction.‡

* Chemie der Gase, Brahmer (1911), 97.

† J. S. C. I., 1911, 746.

‡ See also Frank, U. S. Patent 873,853, Dec. 17, 1907.

CHAPTER XV

HYDROGEN BY THE DECOMPOSITION OF HYDROCARBONS

When methane is heated to 1200° to 1300° C. dissociation occurs and lamp-black and hydrogen are produced. Acetylene is decomposed at a much lower temperature. In general, when subjected to sufficient heat hydrocarbons break down into their elements. This fact has been made use of for the production of hydrogen by decomposing various hydrocarbons and particularly heavy oils. Among the proposals put forward up to the present time are some which relate to the splitting of acetylene or natural gas by passage through the heat zone of an electric arc and separation of the hydrogen from the lamp-black or other carbonaceous material which is formed. The gas may be under pressure to render the decomposition more effective.

Pictet accomplishes this decomposition by treatment of the gas in heated tubes,* as, for instance, an endothermic hydrocarbon, such as acetylene, is passed through a tube, the front portion of which is heated to about 500° C., at which temperature the gas dissociates into its elements with the evolution of a large quantity of heat. The latter raises the temperature of the tube sufficiently to dissociate fresh quantities of acetylene without the further application of external heat. The rear portion of the tube is surrounded by a refrigerating appliance, and the products of decomposition, hydrogen and lamp-black, are passed into a suitable apparatus for their separation. In the same way exothermic hydrocarbons, such as petroleum vapors, mixed with steam may be decomposed with the formation of hydrogen and carbon monoxide; in this case the combination of nascent carbon and oxygen supplies a portion of the heat required by the reaction, the balance which is required to dissociate steam and hydrocarbon being supplied by external heating. By admitting a regulated quantity of oxygen, the combination of the latter with nascent carbon may be made to provide all the heat required by the reaction, it being then only necessary to heat the hydrocarbons initially to their temperature of dissociation. The apparatus may conveniently consist of a steel, iron or porcelain tube, one portion of which is heated by means of a gas furnace, and the other cooled by water, or by a liquid hydrocarbon,

* French Patent 421,838, Oct. 26, 1910.

the vapors of which are afterwards admitted to the tube for their dissociation. The tube is provided with the conduits necessary for the admission of the raw materials and for the withdrawal of the products of dissociation, these conduits being preferably composed of " pure iron " covered with nickel; the lamp-black is separated by washing or by means of filters.

In a modification of the foregoing Pictet (British Patent 14,703, June 21, 1911) operates in such a way that the carbon, instead of being deposited in the form of soot, is converted into carbon monoxide by interaction with water vapor. External heat (39.36 units for every 18 grams of water) is applied for decomposing the water vapor, in addition to that required to decompose the hydrocarbon vapors, for which the temperature is raised substantially to the melting point of iron. Water and hydrocarbon are fed, for example, into an iron tube, which is of sufficient length (say 3 to 4 meters) to enable the supplementary heat to be imparted without damage, and these being vaporized on entry, react in the further end of the tube, which is the more strongly heated; the gas produced is then cooled and passes through a filter to a gas holder, there being a soot chamber and also arrangements for the removal of soot from the tube and filter. Ten liters of petroleum, mixed with 3 to 5.5 liters of water, may be thus decomposed per hour, in the apparatus described, the mixture furnishing approximately 3000 liters of gas for every liter of hydrocarbon, with a calorific value of 3000 to 3600 heat units per cubic meter. By regulating the supply of water, any desired proportion of carbon can be converted into carbon monoxide.

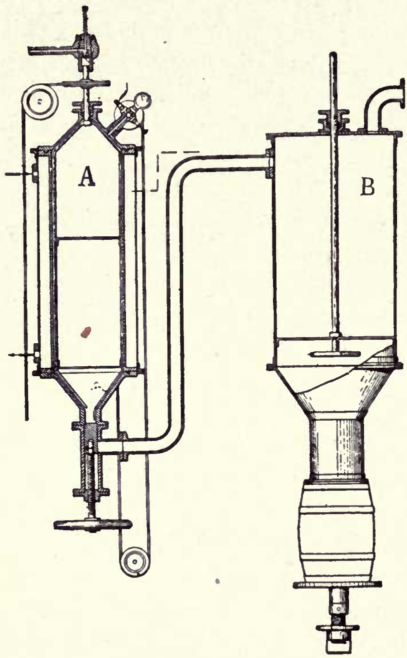


FIG. 67.

In preparing hydrogen from crude petroleum or petroleum tar oils (British Patent 13,397, June 3, 1911) the vapors are heated in such a manner that 18.1 calories are supplied to 16 grams of gas, with a tube temperature of 1200° to 1350° C.

Another process worked out by the **Carbonium Company** in Germany employs acetylene gas which is compressed to two atmospheres and exploded by an electric spark.*

$$C_2H_2 = C_2 + H_2.$$

The acetylene thereby dissociates into the elements carbon and hydro-

* Met. and Chem. Eng. (1911), 157.

gen. The carbon deposits in the form of lamp-black. The hydrogen is passed through large washer and stored. Its degree of purity is exceptionally high. For each cubic meter of hydrogen produced about one kilo of lamp-black is formed. A condition for getting the hydrogen cheaply by this method is that there is a market for the lamp-black.

Wachtolf * compresses the acetylene to about 4 to 6 atmospheres and explodes electrically. In Fig. 67 the explosion chamber is shown on the left and a lamp-black collector on the right. The explosion chamber is provided with a rotary scraper to remove lamp-black adhering to the walls.†

Geisenberger ‡ generates hydrogen alone or mixed with carbon monoxide or carbon dioxide, by the action of heat alone or of heat and steam, on light hydrocarbons, such as benzine, or on other materials containing hydrogen and carbon, e.g., bitumen, shale, beeswax, turpentine, etc. The organic substance is heated in a retort, to which steam may be admitted, to its point of decomposition. The hydrogen is separated from the other gases in the mixture obtained, either by physical means, depending on the differences in density, or by chemical means, such as absorbing the carbon dioxide by means of sodium carbonate or hydroxide solution.

Rincker and **Wolter** § make use of two generators, somewhat resembling those used in making water gas, for the decomposition of oils and tars. These generators are arranged side by side and charged with coke. After they have been raised to incandescence by a blast of air, a charge of tar is introduced into one of them and is partly transformed into gas by the glowing fuel. The gas formed escapes by its own expansion. A current of air is then introduced which carries forward the remaining vapors of tar into the second generator where they are converted into a permanent gas. At the same time the blast of air raises the contents of the first generator to incandescence again, and the process is reversed by introducing the tar into the second generator and repeating the operations in the reverse direction.

In a modified form of the apparatus ‖ the two generators are arranged one above the other and are charged with coke. The coke in the lower generator is ignited and then brought to incandescence by a blast of air which has been preheated by being caused to pass through a jacket surrounding the upper generator. The fuel in the latter is

* German Patent 194,301.

† Decomposition of hydrocarbons under pressure is described by Bosch, German Patent 268,291, July 14, 1911; Chem. Zeit. Rep. (1914), 32.

‡ French Patent 361,492, Dec. 21, 1905.

§ French Patent 391,868, May 11, 1908.

‖ French Patent 391,867, May 11, 1908.

also ignited and then raised to incandescence by natural draught. The products of combustion are allowed to escape to the chimney. When the fuel is glowing brightly, the air supply is cut off and a charge of oil is introduced into the lower generator through pipes in the top. The oil passes over the glowing fuel and is partially converted into permanent gas which escapes through a pipe in the side by its own

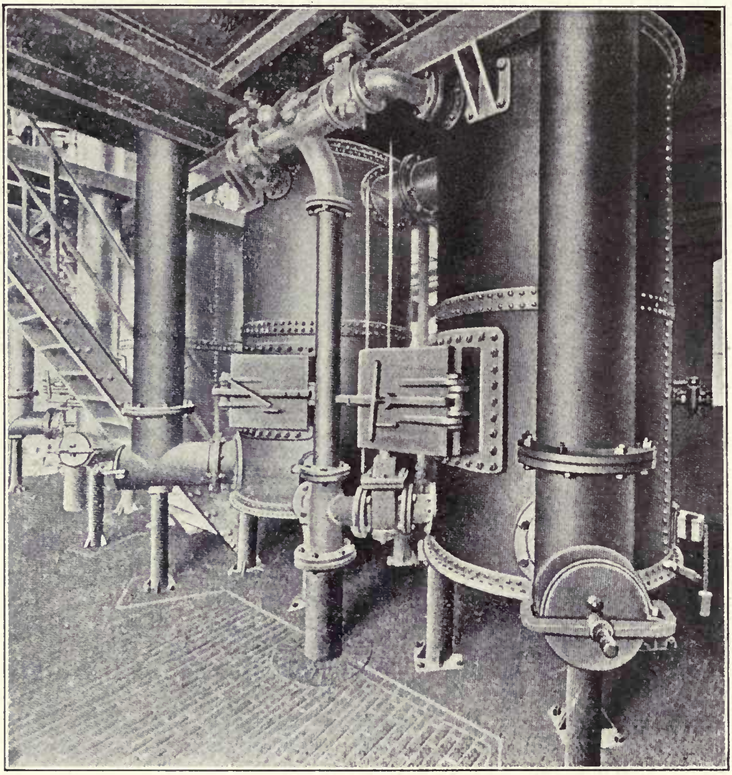


FIG. 68.

expansion. The blast of air is then again turned on, whereby the vapors of oil left in the lower generator are blown into the upper one, where they are gasified and fixed during their passage through the glowing fuel. The lower generator is at the same time again raised to incandescence and the process is repeated.*

* Apparatus for the production of hydrogen by the decomposition of the vapors of oil or tar by exposure to a high temperature is the basis of a patent to the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft, Berlin, German Patent 267,944, Jan. 28, 1913; Chem. Zeit. Rep. (1914), 31.

Equipment for the Rincker-Wolter system is manufactured by the Hollandsche Residugas-Maatschappij of Rotterdam. The gas-making plant consists of twin generators, Fig. 68, lined with firebrick and provided with grate bars and clinkering doors, in short, resembling water-gas generators but lacking a carburettor and superheater. The generators are connected near the top and in the upper part are lids for feeding purposes, which carry sprayers for introduction of the oil.

Fig. 69 shows the operating floor of one of these plants. The generators are

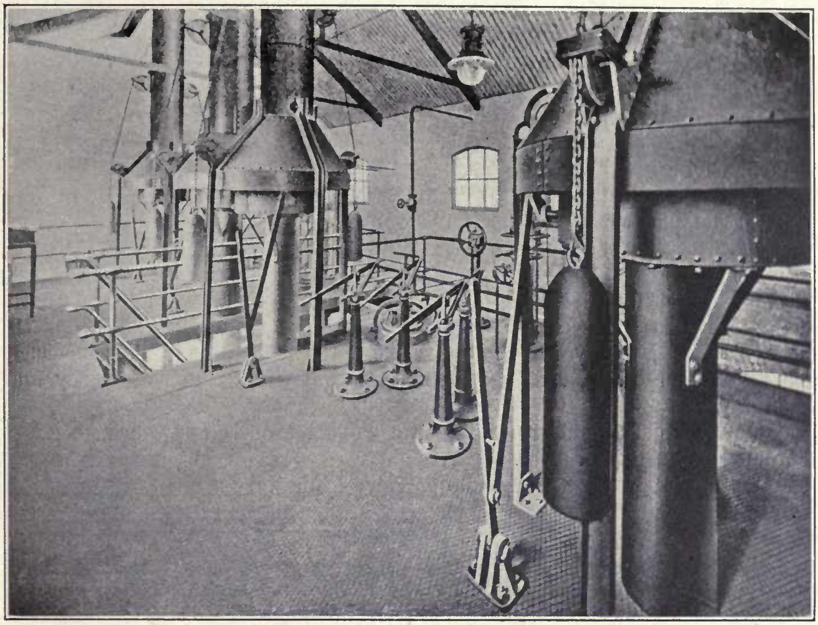


Fig. 69.

equipped with primary and secondary blast pipes, steam inlets and dust collectors. Both generators are charged with coke and fired. The generators are operated alternately in the blowing-run, the first generator receiving the primary, and the second generator the secondary, air blast. Combustion is incomplete in the first generator and the producer gas obtained is led to the second generator where it is burned on meeting the current of secondary air, thus heating up the second generator.

As it is preferable to reach nearly equal temperatures in both generators, the sequence is reversed after a short blowing and the first generator becomes second in the series. When both generators have reached the proper temperature, the air valves are shut and the gas run begins. The temperature of the fuel bed has to be varied somewhat according to the nature of the raw materials. For hydrogen production a temperature of about 1200° C. is required. Too low a temperature gives so impure a gas that subsequent purification of the hydrogen is rendered costly. At the end of the blowing-run oil is sprayed for several minutes on the hot coke and gasification takes place. Immediately after this the sprayer is cleaned by blowing steam through it. The gas formed by decomposition of the oil passes to a seal and from there to scrubbers and purifiers.

Fig. 70 shows the gas outlets and seal. The residue of gas in the generators is expelled by steam. Lamp-black is deposited in the generators and is consumed in the next run. Fig. 71 shows the generators of a plant at Utrecht.

In a well-handled run gas of the following composition is said to be obtained:

	Per cent
H	96
N	1.3
CO	2.7

And by passing this gas over heated soda-lime a gas has been secured analyzing:

	Per cent
H	98.4
N	1.2
CO *	0.4

To avoid difficulties from clinkering of the ash of the fuel, the author has suggested the addition of a small proportion of lime to the charge of coke, so as to flux the ash and thus to enable the maintenance of the requisite high temperature in the fuel bed.†

A method of preparing hydrogen is proposed by the *Badische Anilin und Soda Fabrik* ‡ according to which a mixture of hydrocarbons and steam is passed over an inactive, refractory oxide, such as magnesia, coated with nickel or nickel oxide, at a temperature of 800° to 1000°. The resulting gaseous mixture is freed from carbon monoxide and dioxide, leaving substantially pure hydrogen.

Efforts to secure hydrogen from illuminating gas have met with a considerable measure of success. By the process of **Oechelhauser** hydrogen of about 80 per cent purity is obtained. A gas of much higher hydrogen content has been produced by the Berlin-Anhaltischen Maschinenbau —*A.*—*G.* which is based on investigations made by Bunte. The illuminating gas is first freed of carbon dioxide and is then conducted over white-hot coke which decomposes the hydrocarbons and yields a gas mixture consisting almost entirely of hydrogen, carbon monoxide and nitrogen. The carbon monoxide is removed

* Sanders (Zeitsch. f. angew. Chem. (1912), 2404) states that the cost of hydrogen by the Rincker-Wolter system is 10.5 to 14 pfennig per cubic meter. In a private communication to the author, the manufacturers advise the cost of the smallest equipment they make, having a capacity of 3500 cubic feet of hydrogen per hour, is $2575 plus erecting expenses. With oil at about 4 cents per gallon the hydrogen is estimated to cost about $1.75 per thousand cubic feet.

† Ellis, U. S. Patent, 1,092,903, April 14, 1914.

‡ J. S. C. I., 1914, 313.

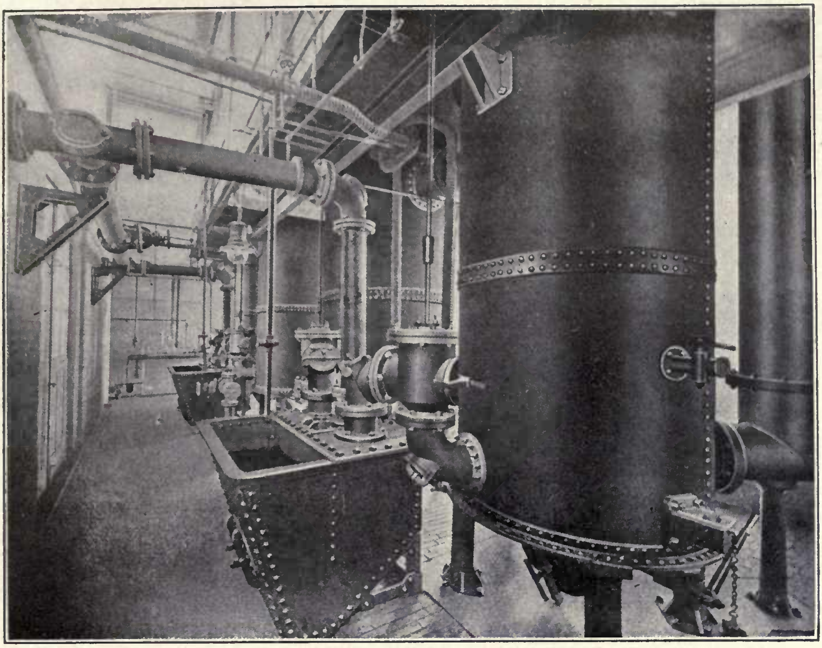


FIG. 70.

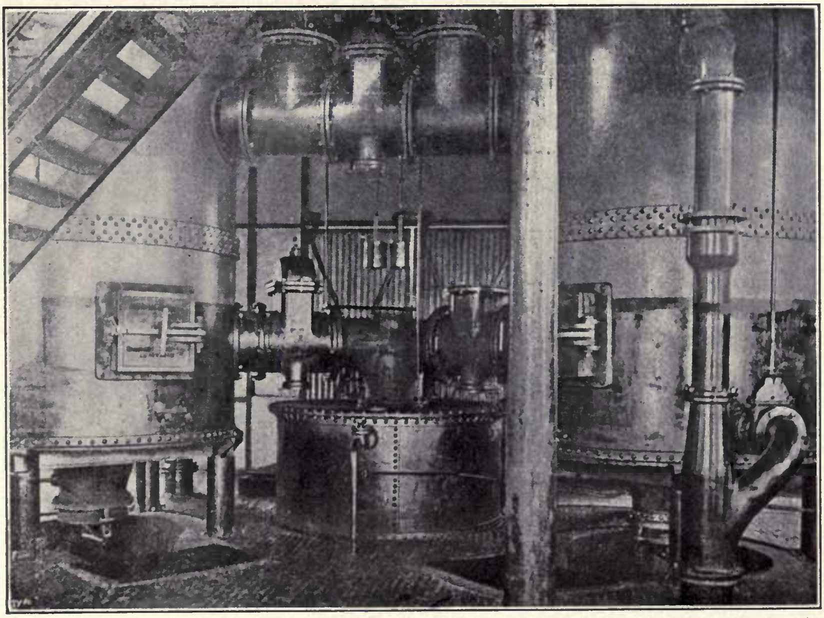


FIG. 71.

by treatment with soda lime and the gas then consists largely of hydrogen with only nitrogen as an impurity. The specific gravity is 0.085 to 0.097 and the gas has been found to be well adapted for most technical purposes. The process can be put in operation at any gas works equipped with a water-gas plant and the installation is not very costly.*

* Sander Zeitsch. f. angew. Chemie (1912), 2406.

CHAPTER XVI

HYDROGEN BY THE ACTION OF STEAM ON HEATED METALS

A large number of proposals for making hydrogen exist which are based on a very old reaction, namely, the passage of steam over red hot iron in a finely-divided state. The main reaction which occurs is

$$3\,Fe + 4\,H_2O = Fe_3O_4 + 4\,H_2.$$

On the large scale it becomes necessary to regenerate the iron material; which is effected by reduction, usually with water gas. With an impure gas slagging difficulties arise. **Giffard** found that the charge of iron soon became inefficient because the sulfur in the gas formed on the iron particles a resistant coating of iron sulfide, which also acted as a flux and caused the iron material to sinter into a coherent mass. Hence prior purification of the reducing gas was found necessary for satisfactory operation. Apart from the sintering effect of sulfur on the iron material, the water gas should be freed from this element as otherwise the hydrogen would take up sulfur and poison the catalyzer. For each cubic foot of hydrogen produced, about three cubic feet of water gas are required. This requires the purification of three volumes of water gas for one volume of hydrogen.

Some of the processes described have had little or no commercial success, but are included because they involve certain features which are suggestive or instructive.

Lewes * prepared hydrogen in the following manner:

A retort, partly filled with iron borings, or with a mixture of iron and carbonaceous material, or with asbestos containing iron in a very fine state of division, is placed in the center of a gas producer. By means of an air blast the fuel in the producer is raised to a bright red heat and then a little steam is admitted together with the air. The gaseous mixture of carbonic oxide, nitrogen and hydrogen produced in this way is led from the top of the producer down through the retort. As soon as the iron oxide in the retort is completely reduced, and the requisite temperature has been attained, the producer gas is turned off and steam, previously heated in the producer, is passed over the iron, the hydrogen being led away to a gasometer. The process is then repeated as described. One of the advantages claimed for this form of apparatus is that the rapid cooling of the iron during the decomposition of the steam is prevented. Lewes claims (British Patent 4134, March 7, 1891) the

* British Patent 20,752, Dec. 19, 1890.

use of a mixture of carbonic oxide, nitrogen and hydrogen for the reduction of oxide of iron in the above process. This gaseous mixture is regarded as a better reducing agent than carbonic oxide, and is easily obtained. The finely-divided iron employed for the production of hydrogen is prepared by saturating asbestos or pumice with certain iron salts, which are easily decomposed into oxide of iron on heating, or by mixing moist hydrated oxide of iron with asbestos fiber and iron filings.

The **Dellwik-Fleischer Wassergas-Ges. m. b. H.*** prepare iron by the reduction of a mineral oxide which retains both porosity and resistance after repeated use. In order to prevent deposition of carbon during the reduction of the iron oxide in the retort, the reducing gas is mixed with a volume of steam equal to at least half the sum of the carbon monoxide and hydrocarbons present in it. It is also found economical to carry the reduction only half way instead of completely to the metal, and this, moreover, gives purer hydrogen since no carbon can be deposited during such partial reduction. In British Patent 7849, of 1909, the Dellwik-Fleischer Co. make use of iron pyrites roasted to expel all sulfur and volatile metals.†

Hydrogen gas is produced according to **Hills** and **Lane** ‡ by passing steam, preferably superheated, over iron contained in heated retorts; and the mixture of hydrogen and steam is led through coolers, from which the hydrogen passes to a gasometer. By means of reversing valves, controlling inlet and outlet passages, a reducing gas, such as water gas, coal gas or the like, is then led through the retorts to reduce the iron oxide formed, and then steam is again passed through. Lane and Monteux § secure the production of pure or nearly pure hydrogen in a continuous manner by the action of steam on red-hot iron. Finely-divided iron is contained in a series of vertical retorts, heated externally by gas, in combination with a regenerative system. The retorts are so connected that a current of steam passes through some, while the iron oxide, already formed, is being reduced in others by a stream of reducing gas sent in the opposite direction. Oxidation and reduction thus take place alternately, oxidation being found to occupy only half the time of reduction. The hydrogen produced is cooled and purified, to remove traces of carbon dioxide, etc. The reducing gas is made in a producer, and by introducing an excess of steam, it becomes rich in hydrogen. The excess of reducing gas is utilized for heating the retorts. After repeated use the iron becomes inactive, owing to an accumulation of impurities, but if these are burned away

* French Patent 395,132, Oct. 10, 1908.

† British Patent 21,479, Oct. 10, 1908, and 7849, April 1, 1909.

‡ British Patent 10,356, May 7, 1903.

§ French Patent 386,991, Feb. 7, 1908.

by the occasional admission of air, the efficiency of the iron is said to be restored.

As it has been found in practice that the reducing reaction takes considerably longer than the generation of hydrogen, the **Lane** process (British Patent 17,591, July 29, 1909) may be carried out in three or more groups of retorts, the greater part of which are constantly subjected to the action of reducing gases for the regeneration of the iron, or other hydrogen-producing substance. The retorts communicate with one another by means of a series of pipes, fitted with controlling valves, so that steam or the reducing gases may be admitted as required. The hydrogen, which is evolved in the first few minutes of the operation, being impure, is diverted from the collector of pure hydrogen, and mixed with the water gas used for reduction. A considerable excess of water gas is used for reduction, and it undergoes a very thorough system of purification before being admitted to the retorts; the excess, which issues, is freed from the accompanying steam and used again. Means are provided for forcing hot air through the reaction chamber, which is done periodically between the two reactions so as to burn out objectionable impurities, especially sulfur. For the purification of the excess of water gas, or other reducing medium, which issues unchanged from the reducing retorts, the gas is passed into a cooler and washer, which removes mechanical impurities, and thence into a compressor. From the latter it passes under a pressure of several atmospheres into a strong receiver. The latter contains coke or the like material, down which cold water is distributed by means of a pump or other forcing device. The compressed gas, coming into contact with cold water, is freed from such impurities as sulfur dioxide, hydrogen sulfide, carbon dioxide, etc., either by solution or by condensation, being at the same time deprived of the greater part of its moisture.*

With the Lane and similar apparatus it has been found † that the hydrogen gas obtained contains a relatively large proportion of gaseous and solid bodies or impurities, produced concurrently with the hydrogen and whose presence considerably increases the quantity of reducing gas necessary for carrying out the reduction operation, as well as the time necessary for effecting the deoxidation of the contact material. The presence of these impurities in the hydrogen gas is due to the fact that the reducing agent contains sulfur, carbon, etc., which either become deposited on the contact material or generate gases such as sulfurous acid, sulfuretted hydrogen or carbon dioxide. After the reduction phase a certain quantity of free reducing gas still remains in the retort, the presence of which contaminates the hydrogen and consequently lessens its commercial value.

Lane, therefore, proposes means for removing the reducing gas as well as the sulfur, carbon and other impurities between the two oxidizing and reducing steps of the process. To this end the retort is provided at each extremity with a multiple-way controlling valve adapted to establish communication between that end of the retort

* Lane, British Patent 11,878, Jan. 29, 1910.

† Lane, U. S. Patent 1,028,366, June 4, 1912.

and any one of three pipes connected respectively at the one end of the retort to a supply of air under pressure, a supply of reducing gas, and a hydrogen receiver, and at the opposite end of the retort respectively to an outlet, a gas-washing and regenerating apparatus, and a supply of steam under pressure.

In Fig. 72 *A* is the retort provided with an inlet *B* at the lower end and an outlet *C* at the upper end, and *F* and *G* are four-way valves which are capable of being rotated by means of hand-wheels *H* and *J* so as to open communication on the one hand between the retort *A* and either the pipe *K* connected to a hydrogen container, a pipe *M* connected to a supply of reducing gas, or a pipe *N* connected to a supply of air under pressure, and on the other hand either with a discharge pipe *O*, a pipe *P* leading to a gas-washing or regenerating apparatus and a pipe *Q* connected to a supply of low-pressure steam. Assuming that the contact material in the retort has been oxidized during the previous hydrogen-producing phase, the sequence of operations is as follows. In the first place the impurities deposited on the contact material during the previous reduction phase, or present in the gaseous state in the retort, are removed by effecting their combustion. This is effected by rotating the valve *G* one-quarter of a revolution so as to admit air under pressure to the lower part of the retort through the pipes *N* and *D*, and rotating valve *F* so as to force out the products of combustion into the atmosphere through the pipes *E* and *O*. The valve *G* is then rotated so as to admit reducing gas to the retort through pipes *M* and *D* and rotating valve *F* so as to open communication between the upper part of the retort and the gas-washing or regenerating apparatus through pipes *E* and *P*. At the completion of the reducing phase the valve *F* is rotated so as to connect the upper part of the retort with the supply of steam under pressure through pipes *Q* and *E*, whereupon the pressure of the steam being greater than that of the reducing gas remaining in the retort, the latter is forced out through pipes *D* and *M* carrying with it the impure hydrogen which has been generated by the action of the steam on the sulfur, carbon, etc., deposited on the contact material. As soon as it is found that the hydrogen passing out through pipe *M* is sufficiently pure the valve *G* is rotated so as to deliver the gas to the hydrogen container, after which, air is then again passed through the retort in the manner previously described.*

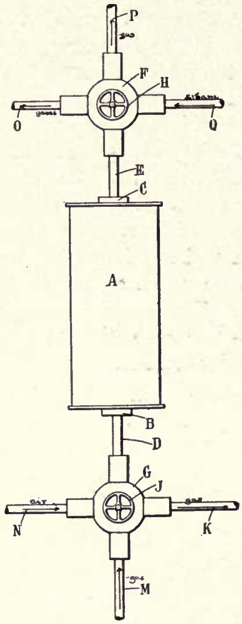


Fig. 72.

* Lane (U. S. Patent 1,040,218, Oct. 1, 1912) purifies the reducing gas in the manufacture of hydrogen by the alternate oxidation and deoxidation of iron, by compressing the reducing gas to a pressure of several atmospheres and then causing it to flow (while still under pressure) in contact with an oppositely flowing stream of water. To increase the effectiveness of the washing operation, the gas is passed through a coke tower through which water is flowing in an opposite direction.

Fig. 73 shows the Lane system as installed in the works of a large soap manufacturer in England. Figs. 74 and 75 show the same system installed at a plant near Paris.

Lane states * that in practice it has been found difficult to obtain pure hydrogen in consequence of the steam admitted to the retort during the oxidation state coming into contact with the reducing gas admitted during the previous reduction state and with the sulfur, carbon, etc., associated with and introduced into the retort by this

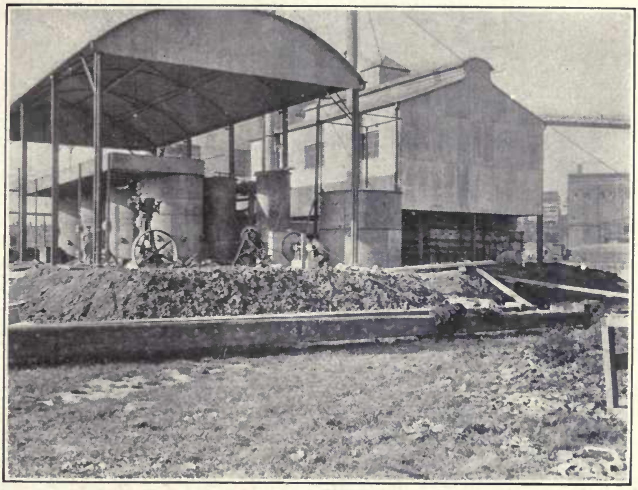


FIG. 73.

gas, the result of which contact being the formation of sulfuretted hydrogen, sulfurous acid, carbon dioxide, etc., and consequent contamination of hydrogen produced by the action of the steam. Lane proposes to remove the sulfur, carbon and other impurities left by the reduction phase, by admitting air under pressure to the retort and discharging the products of combustion into the atmosphere. The admission of air to the retort and the discharge of the products of combustion then ceases and reducing gas is admitted and passed through and out of the retort to a gas-washing and regenerating apparatus. When the reduction stage has been completed the admission of reducing gas is shut off and steam admitted. As a certain proportion of reducing gas will then be present, impure hydrogen will be produced and this is allowed to go to waste, until the product is found to be sufficiently pure. Thereupon the outlet to the atmosphere is closed and the hydrogen passed into a storage tank.

* U. S. Patent 1,078,686, Nov. 18, 1913.

A process devised by **Messerschmitt** * depends upon the alternate oxidation of spongy iron by means of steam, with the evolution of

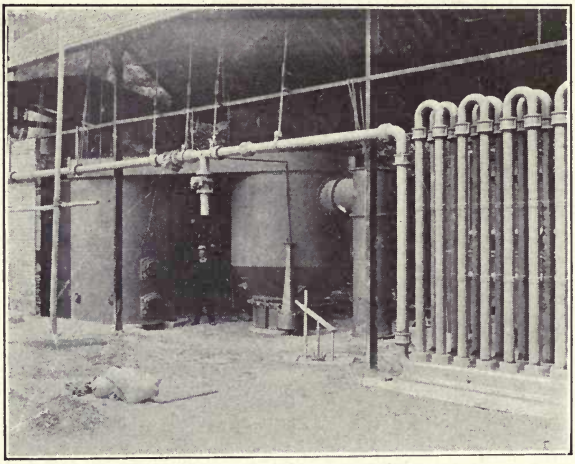


FIG. 74.

hydrogen, and the reduction of the resulting iron oxide † by means of reducing gases, such as water gas.

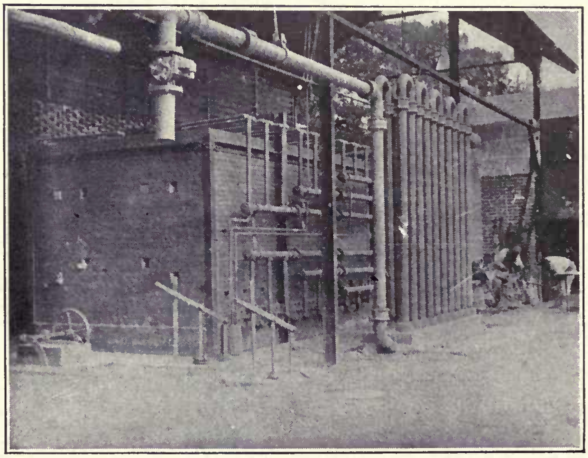


FIG. 75.

* French Patent 444,105, May 22, 1912.

† After iron oxide has been used for a time it becomes partially or wholly inactive and has to be replaced by fresh material. It has been proposed to make the reducing chamber vertical with a grate at the bottom through which the spent oxide may be removed from time to time just as ashes are withdrawn from a gas producer.

An upright, cylindrical reaction chamber made of iron is suspended inside a furnace chamber, with which it is in open communication at the bottom, the lower end of the cylinder being provided with a grate to support the column of reacting material. The width of the reaction cylinder is relatively small, so that the contents may readily be heated from all sides, and the furnace chamber is provided with checkerwork constituting a superheater. Both the reaction cylinder and the furnace chamber are capable of being sealed, and are provided with a system of pipes and valves, enabling the introduction of either steam or water gas into the reaction cylinder or the furnace chamber. An air-supply pipe communicates with the furnace chamber, and a pipe leading from the top of the reaction cylinder can be put into communication with a gas purifier and the steam-raising plant. The process is carried out in three phases; water gas and air are first burned in the furnace chamber until the material inside the reaction cylinder has reached the required temperature. The air supply is then cut off and water gas, flowing in at the bottom of the furnace, becomes strongly heated, enters the open lower end of the cylinder, traverses the mass of iron oxide in an upward direction, and finally passes off at the top to the steam-raising plant, where any combustible gases are utilized. When the reduction of the iron oxide is complete the supply of water gas is cut off and steam is introduced, first into the bottom of the furnace to sweep out any residual gases from the second operation (the furnace being in direct communication with the chimney while this is going on), and then into the top of the furnace chamber, from which it passes downwards through the hot checker-work and finally upwards through the mass of spongy iron. Hydrogen issues from the top of the reaction cylinder and travels through a purifier into a gasometer. The iron receptacle may take the form of two concentric cylinders, the reaction material being in that case charged into the annular space between the two. The cylinders are periodically heated and reduced by means of the reducing gases, both inside and outside.

Messerschmitt has proposed to use compact iron (wrought iron or steel) as a support for spongy iron; only the surface layers of the compact iron taking part in the reaction. The spongy iron may, for example, be placed in the channels of a number of iron bars of U-shaped cross-section, or in perforated moulds, tubes, boxes or troughs of compact iron.*

Elworthy † asserts that the various apparatus proposed for the production of hydrogen by the steam and iron method are subjected to serious drawbacks in practice, owing to the liability of the iron to cake together and to its difficulty of access and removal.

The iron rapidly cakes and chokes, so that the steam or gas comes into contact with only a small proportion of the active surface and loss of efficiency results. It is thus frequently necessary to remove and replenish the iron; but this is a troublesome operation, owing to the construction of the furnace and difficulty of the removal of the iron. Hence Elworthy places the iron in finely-divided form in a large number of separate trays of refractory fire-brick or the like, each adapted to contain a shallow layer of iron in finely-divided form and to be built up in successive layers from bottom to top of the furnace, so as to form a close-lying refractory

* British Patent 12,117, May 22, 1912.

† U. S. Patent 778,182, Dec. 20, 1904.

filling (Fig. 76). The trays are open at their ends to enable the steam or gas to pass freely over them in contact with the iron when built up, and they have supporting flanges for supporting the under face of one tray at a suitable distance from the material on the tray below, and this under face of the tray radiates a quantity of heat onto the shallow layer of metallic iron during the heat-absorbing or oxidizing stage, while at the same time superheating the steam as it passes along the narrow shallow channel between the upper and lower series of trays. When the trays are built up in the furnace, they form a number of narrow flues containing a shallow layer of iron and running in a zigzag course from bottom to top of the furnace and affording free passage for the steam or reducing gas. These narrow flues, so to speak, divide up the mass of refractory material into a cellular structure such that the gases can pass freely through the cell flues over the iron.

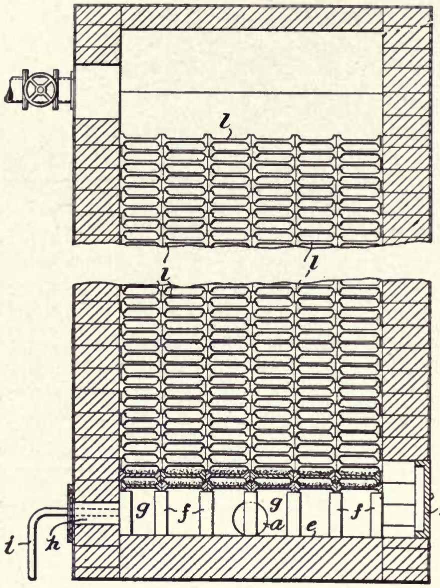


Fig. 76.

Messerschmitt * employs spongy iron produced from fragmentary oxide iron ore (i.e., an ore containing Fe_2O_3). Only spongy iron produced from such oxidized iron ore is regarded by Messerschmitt as possessing the requisite porosity and strength for carrying out the process.

The effect of using ferric oxide as raw material, it is claimed, is that the oxide after reduction becomes porous throughout its entire mass on account of the decrease in volume consequent upon the removal of the oxygen therefrom and thus an increased surface is exposed to the subsequent action of the steam. The use of ferric oxide in the form of oxide ores is important because the lumps of this ore, in consequence of its peculiar natural texture, maintain their shape in spite of repeated reductions and oxidations and the ore possesses the necessary strength to withstand the pressure of superimposed layers; if this were otherwise the path for the gases would become choked by the crumbling of the ferric oxide and continuous working would be impeded. The gangue, clay, silica and other components of the ore have for effect to prevent (in spite of high temperatures which may be produced either intentionally or in consequence of irregular working of the furnace) a sintering of the charge, the latter thus constituting a sort of rigid incombustible carrier for the oxides and the iron sponge.

The presence of carbon monoxide in hydrogen gas-mixtures as at present produced by the action of steam on reduced iron is to be ascribed to the following: If ferric oxide be reduced by means of carbon monoxide metallic iron and carbon dioxide are formed, but simultaneously a considerable quantity of carbon is precipitated from the carbon monoxide. Hence, if after completion of the reduction phase of

* U. S. Patent 971,206 of Sept. 27, 1910.

the process, steam be led over the mixture containing spongy iron thereby produced, there is produced not only hydrogen according to the equation,

$$3\,Fe + 4\,H_2O = Fe_3O_4 + 4\,H_2,$$

but also at the same time carbon monoxide and carbon dioxide resulting from the reaction of the steam on the carbon present, thus contaminating the hydrogen. Since the carbon present is incompletely decomposed by the steam at the comparatively low temperatures used, the carbon increases more and more by the repetition of the cycles (i.e., of the reduction and oxidation phases of the process) and consequently the impurity of the resulting hydrogen becomes greater and greater. From this the necessity of employing means for the prevention of the precipitation of carbon during the reduction phase will be evident. The precipitation of carbon from the heated carbon monoxide takes place, according to the equation,

$$2\,CO = C + CO_2.$$

In order to prevent this precipitation of carbon the following method is used by Messerschmitt:

The gases destined for reduction and containing carbon monoxide and hydrocarbons are mixed with a quantity of steam such that the steam volume amounts, at the most, to half of the volume of the carbon monoxide plus that of the hydrocarbons. For reducing the ferric oxide (or Fe_3O_4) this mixture may be directly led into the retorts or tubes containing the iron oxide without a considerable amount of carbon being precipitated. The reason of this result is explained as follows: If carbon monoxide be mixed with steam, hydrogen and carbon dioxide are formed and the volume of the first is the same as that of the carbon monoxide transformed into dioxide by the oxidation. In place of CO therefore an equal volume of H_2 and an equal volume of CO_2 is formed according to the equation,

$$CO + H_2O = H_2 + CO_2.$$

In general the reaction with hydrocarbons is as follows:

$$CmHn + 2\,mH_2O = 2\,mH_2 + nH + mCO_2.$$

For every volume of hydrocarbon therefore one volume of CO_2 and more than two volumes of hydrogen are formed. Now as only half of the carbon monoxide is oxidized by the steam to CO_2 (since the amount of steam added is only half that of the CO) as final product a gas of the following composition is obtained according to the equation,

$$2\,CO + H_2O = CO + H_2 + CO_2.$$

The gas used for reduction of the iron therefore would yield for every volume of carbon monoxide one volume of hydrogen and one volume of carbon dioxide, or for two volumes of reducing gases one volume of carbon dioxide. This proportion, however, should not be changed on account of the reducing gases because otherwise the reduction of the Fe_3O_4 to metal no longer takes place. For this reason the addition of steam is restricted according to the above equation in order that the gas and steam mixture may be used directly for the reduction of the iron. This reducing gas of the composition $CO + H_2 + CO_2$, however, precipitates considerably less carbon during the reduction than pure carbon monoxide or carbon dioxide mixed with nitrogen (producer gas) would do. The reason for this lies in the presence of the hydrogen. The latter first attacks the ferric oxide with the formation of steam

which again reacts on the carbon monoxide and thus again produces hydrogen and carbon dioxide. By this means the carbon monoxide tending to precipitate carbon is continually reduced, whereas the carbon dioxide and the hydrogen (neither of which precipitates carbon) is increased. From this Messerschmitt concludes that the presence of hydrogen considerably restricts the precipitation of carbon from the carbon monoxide. Hence Messerschmitt proposes to provide for the addition of steam in such manner that its volume only amounts to about half of the combined volume of the carbon monoxide and that of the hydrocarbons contained in the gas.

The reduction of ferric oxides to spongy iron by means of reducing gases takes place very gradually, the iron being gradually reduced to lower stages of oxidation according to the following equations,

$$3\,Fe_2O_3 + CO = 2\,Fe_3O_4 + CO_2,$$
$$2\,Fe_3O_4 + CO = Fe_6O_7 + CO_2,$$
$$Fe_3O_4 + CO = 3\,FeO + CO_2,$$

from which combinations metallic iron is formed by a further reduction according to the equation,

$$Fe_6O_7 + 7\,CO = 3\,Fe_2 + 7\,CO_2.$$

A surplus of reducing gas is necessary in order to render the reduction to spongy iron complete. Since between the products of oxidation (CO_2, H_2O) produced and the reducing gases (CO, H, CnHm) a relationship of equal weights, according to Messerschmitt, subsists which is not affected even by prolonged reaction on the ore, the waste gas of the reduction always contains a considerable amount of reducing gases. The more unfavorable the proportion of undecomposed and decomposed gases in the waste gases becomes, the more difficult it is to reduce the ore. Reduction takes place easily at the beginning, whereas it becomes more difficult as the ore becomes poorer in oxygen and the further reduction to spongy iron has progressed. It is immaterial for the production of the hydrogen whether, during the reduction phase metallic iron or a lower stage of oxidation than that of black oxide of iron is produced, since Fe as well as FeO and Fe_6O_7 for instance are oxidized to Fe_3O_4 when acted on at incandescence by means of steam while giving off hydrogen according to the formula,

$$3\,Fe + 4\,H_2O = Fe_3O_4 + 4\,H_2,$$

or

$$Fe_6O_7 + H_2O = 2\,Fe_3O_4 + H_2.$$

Now it has been found that the proportion of the gases necessary for the reduction relatively to the hydrogen produced during the oxidation phase remains relatively small and that efficient working is secured if the reduction of the ferric oxide (Fe_3O_4) during the reduction phases is only incompletely effected (at most only half reduced).

By the reaction of the steam during the oxidation phase, several gases, methane, carbon dioxide and hydrocarbons, are formed from carbon iron combinations, contaminating the hydrogen. Absorption of carbon is impossible as long as (in addition to spongy iron) a surplus of oxides is contained in the ore. If, for instance, carbon were actually taken up it would of necessity have to be decomposed again by the oxygen of the oxide present, according to the equation,

$$Fe_6O_7 + C = 6\,FeO + CO.$$

A simple form of apparatus devised by Messerschmitt * is shown in Fig. 77. The contact material in this case is iron in the form of tubes. These are shown at *d* in the furnace chamber *f*. The tubes *d* slip over the upright tubes *c* projecting from the top of the distributing chamber *b*. A filling of sand around the base of these tubes *d* seals them and yet allows their ready removal when replacement is required. The reducing gas is introduced by the inlet *a*.†

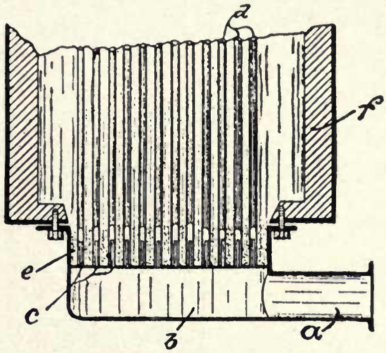


Fig. 77.

In another type of furnace for the production of hydrogen from reduced iron and steam, Messerschmitt ‡ makes use of apparatus as shown in Fig. 78. The reaction is carried out at different planes in this furnace. The walls are provided at different heights with heating channels *cc*. The gas and air nozzles 1, 2, 3 and 4 are so disposed that the heating gases are discharged tangentially into the furnace in such a manner as to prevent local overheating of the iron. The oxidized iron in the different zones of the furnace is successively reduced and heated and the waste gases from one zone are burned by the aid of a blast of air in a higher zone. In the upper part of the structure the checkerwork *g* enables preheating of the reducing gas and steam.

Natural ores of manganese or of manganese and iron are employed by Messerschmitt § in place of ordinary iron ore. It is stated that hydrogen is obtained in good yields at 700° to 800° C. or about 200 degrees lower than with iron sponge.

* Chem. Ztg. Rep. (1913), 521.

† A description of apparatus recently recommended by Messerschmitt appears in Chem. Zeit. Rep. (1913), 696. (German Patents 266,863, July 9, 1911, and 267,594, Feb. 9, 1912.) Messerschmitt has also taken out German Patent 268,339, Oct. 18, 1912, supplementing patent No. 267,594. (Chem. Zeit. Rep. (1914), 31.) A method for the manufacture of hydrogen by the alternate oxidation and reduction of iron is described by Messerschmitt in German Patent 268,062, Nov. 3, 1912. (Chem. Zeit. Rep. (1914), 22, and Zeitsch. f. angew. Chem. (1914), 47, No. 5; (1914), 61, No. 7.) See also German Patent 263,390, July 24, 1912.

‡ Chem. Zeit. Rep. (1913), 521; German Patent 263,391, July 26, 1912.

§ J. S. C. I., 1914, 201; French Patent 461,480, Aug. 19, 1913. Additional methods employed by Messerschmitt for the generation of hydrogen are described in J. S. C. I., 1914, 313.

An apparatus employed by the **Internationale Wasserstoff-Aktien-Gesellschaft** is shown in Fig. 79. On the left is a gas producer supplying fuel gas to heat the two vertical retorts shown on the right. The heating gases and products of combustion move in the direction indicated by the arrows and finally pass to an exit flue. The valves

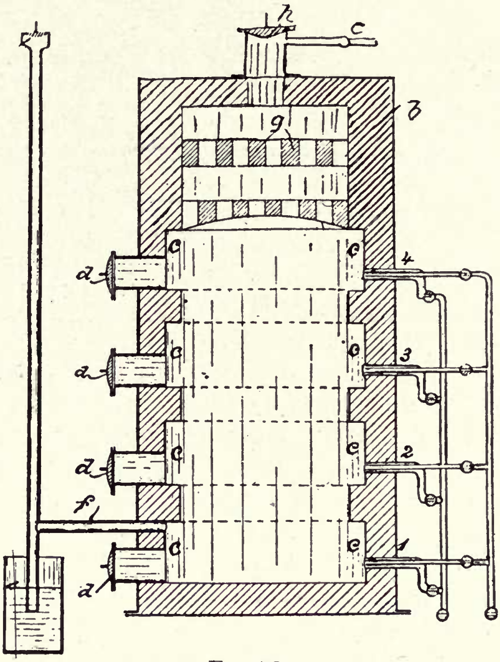


FIG. 78.

a and *b* are opened and water gas flows through the iron ore filling the retorts, reducing iron oxide to finely-divided metallic iron. When reduction has sufficiently progressed the valves *a* and *b* are closed and the three-way valve *c* is opened. Steam is admitted by the valve *d* and hydrogen is withdrawn at *e*. When the iron becomes reoxidized the steam is shut off and the oxide again reduced by water gas. The reducing gases after passage through the retorts are burned in the combustion chamber. The hydrogen exhibits a purity approaching 98 per cent at a cost of 4 cents per cubic meter.*

The above concern † employs iron pyrites waste as raw material,

* Chemie der Gase, Brahmer, Frankfort (1911), 93.

† It should be stated that the Internationale Wasserstoff-Aktiengesellschaft of Germany is the owner of a considerable number of processes and patents (Iwag System) on the production of hydrogen.

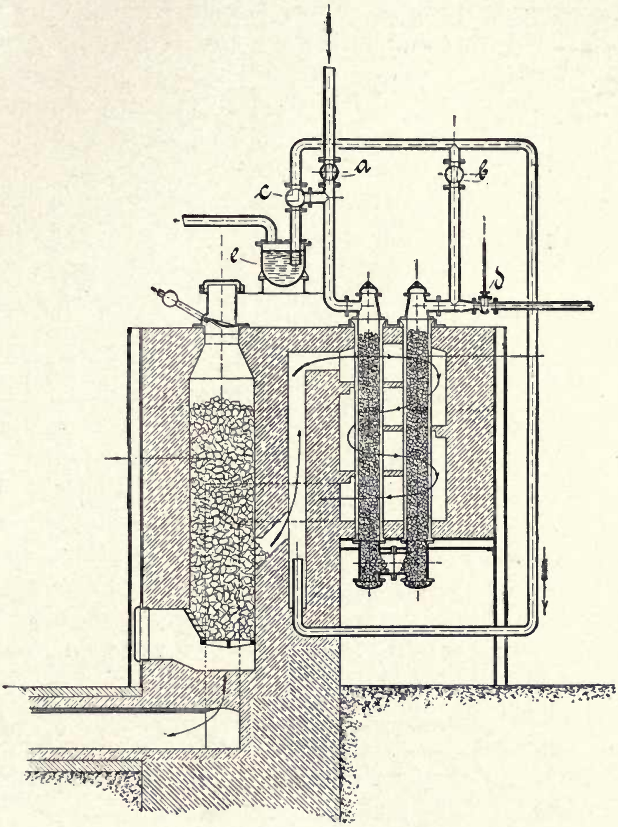


FIG. 79.

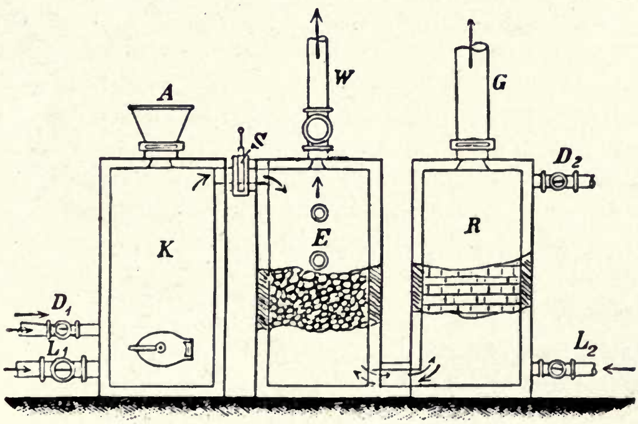


FIG. 80.

which has been deprived of sulfur, arsenic and zinc by roasting; this material is porous and refractory and retains these properties after repeated use.*

By another process a ferruginous mass is treated alternately with steam and a purified reducing gas, both of which are preheated in regenerators situated outside the reaction furnace, so as practically to avoid transference of heat by conduction from these to the furnace. The reducing gas leaving the reaction furnace is burned with oxygen or air in the regenerators, and the process may be made continuous by employing two or more regenerators with a central furnace, and passing steam and gas through the system, first in one and then in the opposite direction.†

In Fig. 80 is shown a hydrogen-generating apparatus designed by **Strache.**‡ *K* is a gas producer, the gas from which passes through the reaction chamber *E*, containing iron filings, and is burned in the checkerwork *R*. On passing steam through the checkerwork in a reverse direction the steam becomes superheated and when brought into contact with the iron filings in *E* hydrogen is produced and is withdrawn at *W*. Another apparatus designed by Strache § is shown in Fig. 81. The water-gas generator 2, provided with inlets 25 and 4, for steam and air respectively is connected with the reaction chamber 6, by the pipe 5, provided with a gas-discharge pipe 24. Just above the place where the pipe 5 enters the reaction chamber is a baffle 22, and on the opposite side of the chamber is a similar baffle 23. A branch from the air-supply pipe opens just below the baffle 22, and similar branches open at 8 and 9. The reaction chamber 6 is divided into compartments by gratings on which the iron reaction material is placed. In the upper part of the chamber, above a regenerator 10, are purifying retorts 11, the gas to be purified entering by 20 and the purified product leaving by 21. When the apparatus has been brought to the proper temperature and is ready for the production of hydrogen, steam is introduced through the pipe 14, below the valve 13, so as to displace any gases from the pipe 5 and the ash-pit 15. Steam is then introduced through the tube 18, below the valve 12, displacing gas from the reaction chamber from the top downwards. The hydrogen produced passes away through 19 to a holder, from which it may be passed through the pipe 20 into the purifying retorts 11, charged with potash lime.

* French Patent 405,200, July 19, 1909.

† British Patent 2096, Jan. 25, 1913, Badische Anilin und Soda Fabrik.

‡ Brahmer, Chemie der Gase, 91.

§ German Patent 253,705, Oct. 26, 1910.

The claim is made by **Dieffenbach** and **Moldenhauer** * for the use of the residue left on roasting spathic iron ore in the air, in the preparation of iron to be employed in the decomposition of steam. This material is very porous, and is in most cases free from substances which would have injurious effects in the manufacture of hydrogen. They also claim † the use of alloys of iron with manganese, chromium, tungsten, titanium, aluminium or other similar elements as the primary materials. These have the advantage that they are not fusible, do

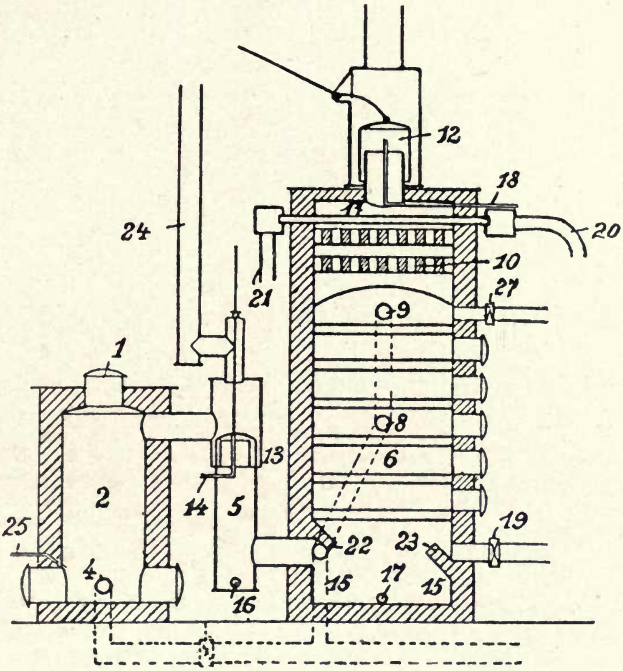


Fig. 81.

not soften, and do not form fusible or soft compounds with iron or its oxides. In place of alloys, mixtures of iron or its oxides with the other elements specified, or their oxides, may be employed, for instance in the form of briquettes.

In the preparation of hydrogen by the alternate action of steam on iron and of reducing gases on ferric oxide, the iron soon loses its activity owing to fritting, etc. The **Badische Anilin und Soda Fabrik** ‡ claim

* German Patent 232,347, Feb. 6, 1910.

† French Patent 444,044, May 20, 1912. See also Zeitsch. f. angew. Chem., 1914, No. 25, 222.

‡ French Patent 440,780, Feb. 29, 1912.

as remedies: the use of fused iron oxides, especially in conjunction with refractory and difficultly reducible oxides of high melting-point such as magnesia or zirconia, the iron oxides being prepared by the fusion of metallic iron in the presence of air or an oxidizing agent; fused iron oxides may be used in conjunction with a silicate as well as similar naturally occurring minerals such as magnetite. The Badische Anilin und Soda Fabrik * also recommend spongy iron prepared by the reduction of minerals or oxides of iron by means of carbon, employing external heating. The metal is said to retain its porosity after repeated use. "Spongy Swedish iron," prepared in the above manner, is especially suitable.

The Berlin-Anhaltische Maschinenbau-A-G.† has an apparatus for making hydrogen by the iron-sponge system which considerably facilitates the handling of the ore and the regulation of the temperature.

Belou ‡ prepares hydrogen by causing steam (preferably superheated) to pass over red-hot iron in retorts. Hydrogen and oxide of iron are thus formed. The hydrogen passes on to a gas holder for use, and the oxide is reduced to metallic iron again by the introduction of charcoal dust. This latter operation generates so much heat that the retort is again immediately ready for decomposing steam. By using a number of retorts and carrying on the two processes of decomposition and revivification alternately, the production of hydrogen may be made continuous. Suitable provision is made for the removal of the carbon monoxide and dioxide formed during the revivification.

Highly-heated tubes of refractory earthenware, partly filled with iron filings, and in which a partial vacuum has been previously produced, are used by **Oettli** (British Patent 16,759, Sept. 4, 1885). A certain proportion of hydrogen is added to the steam, and this, together with the action of the iron filings, is claimed to tend to destroy the equilibrium conditions and to prevent the hydrogen formed by the decomposition of the steam from re-uniting with oxygen. This effect is said to be promoted by the reduced pressure in the tubes, and by the loss of heat due to the splitting up of the aqueous vapor. From the tubes the gases pass through separators to gas holders.

Vignon's apparatus § consists of a set of retorts containing iron oxide. A reducing gas is led from a gas producer, through a suitable purifier, into the retorts for the reduction of the iron oxide. The heat formed thereby is utilized for the regenerative heating of the air blast for the producer. The heat of the hydrogen gas produced is used for superheating the steam. A set of four valves can be manipulated

* French Patent 453,077, Jan. 11, 1913.

† J. S. C. I., 1914, 256, and British Patent, 28,390, Dec. 9, 1913.

‡ British Patent 7518, May 25, 1887.

§ First Addition, dated Dec. 27, 1907, and French Patent 373,271, Jan. 2, 1907.

by a single handle, allowing the regulating and reversing of the different gas currents.

The process of **Gerhartz** * consists in blowing steam through a molten oxidizable metal, and subsequently reducing the oxidized metal for further use. Molten iron, for example, is introduced into a vessel lined with refractory material and provided with a perforated false bottom somewhat after the manner of the Bessemer converter. Steam under pressure is blown into the space below the false bottom and is decomposed while rising through the molten iron; the hydrogen produced is led off through a suitable pipe, and the heat carried by it is utilized for generating steam. The fluidity of the molten iron is gradually diminished, and after a time the supply of steam is stopped, coke is introduced and the melt is blown with air in order to reduce the iron oxide which has been formed and thus restore the fluidity of the molten mass.

A process brought forward by The Nitrogen Co.† involves reacting with steam on a molten or heated metal having a strong affinity for oxygen, which is thus absorbed. After collecting the residual hydrogen, the metallic oxide produced is made to dissolve or disseminate in a body of fused salt in which it is brought into contact with a suitable reducing agent, the reduced metal being continuously returned for re-oxidation in the process.

Illuminating gas, water gas or other gas containing free hydrogen, according to **Jaubert,** is passed through retorts packed with briquettes formed of iron oxide with a refractory substance and a catalytic agent, the retorts being heated to 800° to 900° C.‡ Steam is afterwards passed through the retorts at the same temperature, yielding hydrogen. The briquettes are preferably composed of a mixture of 30 to 60 kilos of iron oxide (Fe_2O_3 or Fe_3O_4), 15 to 25 kilos of fire clay or pumice, 15 to 25 kilos of calcined magnesia and 5 to 15 kilos of the oxide of lead copper, chromium or manganese.

The decomposition of water into hydrogen and oxygen by the action of concentrated solar rays in presence of finely-divided iron and apparatus for effecting this is described by Claver.§

In the manufacture of hydrogen by alternately passing steam over iron, and water gas over the iron oxide thus formed, **Caro** ‖ has devised a system by which portions of the water gas are burned in different

* German Patent 226,543, June 23, 1909.

† British Patent 17,666, Aug. 3, 1911.

‡ Jaubert, French Patent 418,312, Sept. 23, 1909.

§ British Patent 21,468, Nov. 12, 1895.

‖ German Patent 249,269, Aug. 30, 1910.

parts of the reaction chamber, so that in addition to the reduction of the iron oxide, a superheating of the reduced iron is effected. It is claimed that by working in this manner, the gas-making period can be considerably prolonged.

Steam and hydrocarbons (such as those derived from iron carbides) are passed over red-hot iron which has been mixed with (preferably 5 to 10 per cent of) copper, lead, vanadium or aluminium, either together or separately. These metals according to **Saubermann** * catalytically accelerate the reaction between steam and iron, and also decompose the hydrocarbons.

The action of mixtures of carbon monoxide and hydrogen on iron oxides is discussed by **Gautier** and **Clausmann.**† They passed a mixture of 3 volumes of carbon monoxide and 1 volume of hydrogen at 500° C. over the ferroso-ferric oxide derived from the calcination of a native ferrous carbonate. The substance formed contained about 7 per cent of carbon, and 93 per cent of ferrous oxide and iron carbides in approximately equal proportions. When steam was passed over this substance at 400° C., a gas was obtained containing 96 per cent of hydrogen and 4 per cent of methane. Over iron (reduced from the oxalate spread over pumice) at 1250° C. was passed a mixture of 2 volumes of carbon dioxide and 1 volume of hydrogen. The issuing gas, besides 23 per cent of carbon monoxide and 76 per cent of hydrogen, contained 0.15 per cent methane.

* British Patent 401, Jan. 6, 1911.

† Compt. rend. (1910), **151**, 355.

CHAPTER XVII

ACTION OF ACIDS ON METALS

One of the oldest methods of generating hydrogen and one which is to-day commonly used in the laboratory and for the production of hydrogen on the small scale is that of acting on metals with acids, iron or zinc and sulfuric acid being the materials usually employed. The cost of generation in this manner is too high to permit of large scale operations except in those cases where hydrogen is obtained as a by-product in the preparation of metallic salts. Accordingly this method of hydrogen generation will be considered only very briefly.

Carulla endeavors to prepare alkali salts, hydrogen and iron oxide, the gas being generated by the action of hydrochloric acid on iron. Instead of using water alone for the absorption of hydrochloric acid in the Le Blanc process, some or all of the receivers or towers are packed with scrap iron or mild steel, ferrous chloride being thus formed and hydrogen evolved. The chloride is then converted, by precipitation, into iron oxide * and, since very dilute solutions are preferable for this purpose, the absorption of the last traces of hydrochloric acid is rendered very easy by this process, the ferrous liquor plant being conveniently placed at the end of the system, and hydrochloric acid of high strength being produced, if desired, in intermediate parts of the plant.

According to **Barton** † dilute sulfuric acid is allowed to act on zinc and the zinc sulfate solution produced is filtered and mixed with a solution of sodium carbonate or bicarbonate, thus giving a precipitate which is separated, washed and dried, and sodium sulfate which is also recovered.

The insoluble zinc precipitate is proposed as "an excellent substitute for oxide of zinc used in the paint and rubber industries." The apparatus claimed consists of a generating vessel, communicating with an acid tank by a feed pipe and a return pipe, and also with a gasometer and a mixing tank, the latter receiving the zinc sulfate solution from the generator and sodium carbonate solution from another vessel and communicating, in its turn, with a centrifugal separating and washing apparatus. The generator may be fitted with electrodes for the production of electrical energy.

* e. g., as in British Patent 27,302, 1908; J. S. C. I., 1909, 1126.

† British Patent 28,534, Dec. 8, 1910.

An apparatus arranged to generate electrical energy when zinc is being dissolved in sulfuric acid to produce hydrogen is set forth by **Eastwick** (British Patent 10,228, April 27, 1911). The apparatus, which is intended specially for the generation of hydrogen by the action of zinc on dilute sulfuric acid, consists of a generating chamber, with false bottom, on which rests the metal to be acted upon, and a liquid-collecting chamber situated below. The acid is delivered by gravitation into contact with the metal at a point near to, but above, the false bottom, and the salt solution produced runs through into the collecting chamber. An electrode may, if desired, be immersed in the liquid, within or below the reaction chamber, so that the apparatus may serve also as an electric cell. An apparatus described by way of example comprises superposed chambers contained within a single casing, the uppermost (containing zinc) and the intermediate chamber being provided with porous or perforated false bottoms. Acid is conducted to the first chamber by a pipe which reaches down through the upper layers of zinc into a cage having lateral perforations, and any excess of pressure forces the acid back in the supply pipe, but the zinc sulfate solution produced percolates into the lowermost chamber. A zinc rod or plate, to act as electrode, is placed above the false bottom in the first chamber and a copper electrode in the intermediate chamber, so that, with the descending liquid, an electric cell, suitable for electro-plating work, etc., is produced, this also ensuring the decomposition of any free acid in the spent liquid.

Hydrogen gas is obtained by **Pratis** and **Marengo** * by acting upon iron filings and water by gradual additions of sulfuric acid of 50° Bé., equal parts by weight being taken of each. The hydrogen produced is conducted first through water, then through a solution of a lead salt, and through a device containing diaphragms of wire gauze, to a gasometer, whence the gas traverses an insulating water valve, an elastic chamber and a second device similar to the first, when it is taken by branch pipes to the place of utilization. The arrangements described permit of the gas being produced under considerable pressure.

To overcome the difficulties in the way of generating hydrogen from sulfuric acid and iron, Pratis and Marengo (British Patent 15,509, June 29, 1907) propose to employ the following approximate proportions, by weight:

Broken iron, 5 parts; water, 5 parts; 50° Bé. sulfuric acid, 5.8 parts; these being found to produce a pasty non-caking residue, easy to remove from the apparatus and to work up for the manufacture of ferrous sulfate or Nordhausen sulfuric acid.

The apparatus consists of a generating cylinder, fitted with a valve for discharging the residue. The acid and water are run in on to the charge of iron from reservoirs at a higher level, the supply valve being controlled by the bell of the gas holder, and is self-closing when the bell sinks below a certain level; or, if the gas is to be collected in receivers at high pressure, the full charge of liquids may be added at once. Purifiers are arranged between the generator and gas holder, and an excessive rate of generation is prevented by gas checks, which cause an increase of pressure in the generator, whereby the acid is driven back in the supply pipe and the evolution of gas diminished.

* British Patent 16,277, July 22, 1896.

The reaction which takes place in the spontaneous formation of iron rust,

$$CO_2 + H_2O + Fe + FeCO_3 + H_2$$

may be accelerated by agitation, etc., so as to become a practicable method according to **Bruno** * for the production of hydrogen. Fragments of cast iron or steel or iron filings were introduced together with water into a steel bottle and carbon dioxide was passed in until the air was displaced and the liquid was saturated with the gas. The bottle was then closed by a steel cover, and placed in an apparatus where it made about 2000 revolutions per hour. There was no appreciable change in the pressure inside the vessel, and after 36 to 40 hours the gas withdrawn from the bottle consisted of pure hydrogen. At the end of 20 hours the gas consisted of about two-thirds of hydrogen and one-third of carbon dioxide.

* Bull. Soc. Chim. (1907), 1, 661.

CHAPTER XVIII

MISCELLANEOUS METHODS OF HYDROGEN GENERATION

Much attention has been given to the production of hydrogen by chemicals, which, when added to water or hydrated substances, would liberate hydrogen freely, thus enabling the generation of hydrogen at any point without the necessity of setting up elaborate apparatus. Powdered aluminium or silicon and alkali, "activated" aluminium and water, ferrosilicon and calcium hydrate, calcium hydride and the like have been proposed under various names such as hydrone, hydrogenite, the Hydrik process, etc. Bergius has brought out a novel process involving the treatment of carbon or iron with water in a liquid condition under very high pressures. The following indicate the principal developments in this direction.

Foersterling and **Philipp** * generate hydrogen by causing water, in a finely-divided state, to react successively with relatively small masses of sodium, separated from each other, in the same containing vessel, in such a way that the supply of hydrogen is continuous, and at a rate that substantially prevents a solution being formed. They also propose silicides for the generation of hydrogen.† An intimate mixture of equal parts by weight of sodium and aluminium silicide ("sical") is prepared by heating the two substances in a kneading machine until all the sodium is molten; the kneading appliance is then put into operation and kept continuously rotating while the mixture cools down, after which the latter is transferred to a press and briquetted. One kilo of the mixture, when acted on by water, generates about 700 liters of hydrogen, the reaction being represented by the equation,

$$Al_2Si_4 + 8\,Na + 18\,H_2O = Al_2(OH)_6 + 4\,Na_2SiO_3 + 15\,H_2.$$

Brindley and **Bennie** (U. S. Patent 943,036, Sept. 14, 1909) use a mixture consisting of finely-divided aluminium and molten sodium hydroxide, the proportion of the latter being between 1 and 3 mols. to 1 mol. of aluminium. Silicon and zinc may also be added.

Brindley (U. S. Patent 909,536, Jan. 12, 1909) treats an alkali or alkaline-earth metal, for example sodium, in a finely-divided state, with a crude hydrocarbon oil

* U. S. Patent 883,531, March 31, 1908.

† U. S. Patent 977,442, Dec. 6, 1910.

or similar substance, which will temporarily prevent oxidation of the metal, and with an inert substance such as infusorial earth, and the mixture is compressed into tablets or briquettes, which when brought into contact with water will generate hydrogen. In order to increase the yield of hydrogen, a metal (aluminium, silicon) which forms a hydroxide, the hydrogen of which can be replaced by an alkali or alkaline-earth metal, is also incorporated in the mixture.

Philipp (U. S. Patent 1,041,865, Oct. 22, 1912) generates hydrogen by the action of water on a mixture of metallic sodium and aluminium silicide. The action of water on this mixture does not proceed to completion, and the method consists in first treating the mixture with water, and then passing the hot hydrogen and steam through a similar mixture which has previously been partially decomposed by treatment with water.

Jaubert * suggests that the hydrogen evolved in such industrial processes as the production of electrolytic soda, be collected, deprived of any oxygen present (as by passage over red-hot copper), dried, directed into an iron tube charged with calcium in small pieces, and heated for some hours to redness. The dark grey calcium hydride thus obtained is preserved in closed vessels. When the hydride is brought into contact with cold water, there is a violent evolution of hydrogen.

Bamberger, Bock and **Wanz** † generate hydrogen from calcium hydride which is mixed with substances such as gypsum, sodium bicarbonate, soda-lime or boric acid, which contain water or carbonic acid, but which react only when heated to about 80° C., or a higher temperature.

Gases which are prepared by the action of a liquid upon a solid, for instance, hydrogen by the action of water on calcium hydride, are obtained pure and free from the water vapor which is frequently generated by the heat of the reaction, in the following manner: The solid is placed in a connected series of separate vessels, or in superposed compartments of the same vessel, and the liquid is admitted to the first, or lowest, of the series. The gas given off, along with some vapor of the liquid, passes through the next vessel, or compartment, and so through the series and leaves the last in a dry condition, the water vapor having been retained by the fresh material. When the first vessel is exhausted it is recharged and connected to the end of the series, the second vessel becoming the first. In this way the process becomes continuous.‡

Schwarz § describes two simple methods for preparing pure hydrogen gas and carbonic oxide. On heating a mixture of zinc dust and calcium hydrate gradually in a combustion tube, a constant current of pure hydrogen is liberated according to the equation,

$$Zn + CaH_2O_2 = ZnO + CaO + H_2.$$

* French Patent 327,878, Dec. 31, 1902.

† German Patent 218,257, March 31, 1908.

‡ Jaubert, French Patent 381,605, Nov. 14, 1907.

§ Ber., 19, 1140.

On mixing the zinc dust with calcium carbonate in molecular proportions and heating as before, pure carbonic oxide gas is evolved thus:

$$Zn + CaCO_3 = ZnO + CaO + CO.$$

In both cases nearly theoretical quantities of gas are obtained.

Hydrogen is produced by the process of **Jaubert** * by ignition and autocombustion in a closed generator, of a mixture consisting of an excess of a combustible substance (metal, metalloid or alloy), capable of decomposing steam at a high temperature, an oxidizer or other substance to maintain the combustion, and a substance evolving steam on heating (which is omitted, partially or wholly, if steam be introduced from an external source).

Suitable mixtures, which may be packed in metal cartridges, to be opened and placed directly in the generator, are the following: (*a*) Powdered iron 20 kilos, slaked lime 10, potassium perchlorate 6, (*b*) ferrosilicon, with 75 per cent of silicon, 20, litharge 10, soda-lime, containing two-thirds of sodium hydroxide 60; (*c*) ferrosilicon 20, powdered iron 5, wheat flour 3, lime 5, and potassium chlorate 3. If the ingredient evolving steam be omitted, the generator may be surrounded by a water jacket, the two vessels being connected so that the necessary steam is supplied from the latter by the heat of the reaction; a pipe from the generator conveys the gas either to the exterior or through a purifying and drying apparatus, to be utilized. The generator described is closed by a heavy lid which, for safety, is held in position by its own weight.

The **Hydrogenit** process of Jaubert † involves mixing finely-powdered ferrosilicon with soda-lime to produce a grayish granular mass which easily ignites and burns readily even with the exclusion of air, the reaction being

$$Si + Ca(OH)_2 2\,NaOH = Na_2SiO_3CaO + 2\,H_2.$$

From 3 kilos of the mixture, which, by the way, is stable at ordinary temperature, about 1 cubic meter of very pure hydrogen is obtained. The mixture is pressed to blocks and is shipped in metal containers holding 25 to 50 kilos, affording 8 to 16 cubic meters hydrogen in about a ten-minute period. The mixture is kindled by a small amount of ignition powder or quick-match. Equipments for furnishing 150 cubic meters hydrogen per hour have been made. The generators are arranged in pairs, see Fig. 82.

A case of hydrogenit is placed in each generator. The cover of the generator is put on and clamped in place and the mixture lighted through a closable opening in the cover. The generators are equipped with water jackets and the steam produced by the heat of the reaction is, towards the end of the run, turned into the

* French Patent 427,191, May 21, 1910.

† German Patent 236,974.

generator, giving a larger yield of hydrogen. The gas is washed and dried. One cubic meter of hydrogen made from Hydrogenit costs about 32 to 38 cents.*

Jaubert (French Patent 422,296, Jan. 14, 1910) has described the following modification of the above. Metals such as aluminium or zinc, or their alloys, or metalloids such as silicon or carbon, or their compounds, e.g., ferrosilicon, when mixed with alkali or alkaline-earth hydroxides in the form of dry powders, yield mixtures quite stable at ordinary temperatures. If, however, reaction be induced by local application of heat, hydrogen is evolved and sufficient heat is developed to cause the propagation of the reaction throughout the mass. A suitable appara-

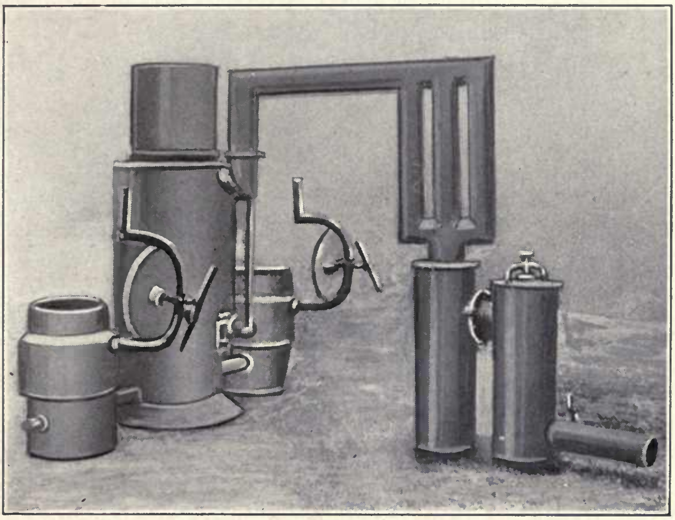


Fig. 82.

tus consists of a tube closed at one end by a screw cap and having near this end an opening (with a screw cap) through which a quick-match or piece of hot iron may be introduced to induce the commencement of the reaction. The other end of the tube is formed by a perforated plate, through which the hydrogen evolved passes into a chamber packed with filtering material, and thence into an annular space formed between the tube and a jacket extending nearly the whole length of the latter. The hydrogen accumulates in this annular space under pressure, and is withdrawn as required through a suitable outlet.

Ferrosilicon containing 75 per cent of silicon, when heated to a very high temperature is capable of decomposing steam with sufficient evolution of heat to carry on the reaction,

$$3\,FeSi_6 + 40\,H_2O = Fe_3O_4 + 18\,SiO_2 + 40\,H_2.$$

(Jaubert, French Patent 438,021, March 4, 1911.) The reaction may be regulated by the addition of lime, which has the further advantage of forming an easily-workable slag. The apparatus comprises a refractory chamber surrounded by a steam coil, the delivery end of which terminates in a series of injectors, which admit steam

* Zeitsch. f. angew. Chem. (1912), 2405.

into the chamber; a feeding hopper is provided at the top of the chamber and a door for the withdrawal of the slag at the bottom.

An alkali or alkaline-earth hydroxide, or a mixture of the two, is mixed with charcoal and a finely-divided metal or mixture of metals, and the whole is heated in a hermetically-sealed vessel, with the exclusion of air, and under diminished pressure. Under the action of the metal, according to Hlavati (German Patent 250,128, Feb. 25, 1911) the hydroxide is converted into oxide, and hydrogen and carbon monoxide are formed.

The **Siemens & Schuckert Company** has worked out a process for the production of hydrogen from the reaction between silicon and caustic soda solution. Formerly steam was employed, but now the heat set free during the reaction is utilized for maintaining the proper conditions. The evolution of hydrogen gas takes place when a 25 per cent solution of caustic soda acts on silicon introduced in small quantities. The capacity of a transportable plant is 60 to 120 cubic meters per hour, while stationary plants are built for capacities up to 300 cubic meters per hour. The process is a neat one, but the cost is about 18.75 cents per cubic meter.*

A somewhat similar system is used in France under the name of the **Silicol** process. Ferrosilicon or other silicon alloy is treated with freshly-prepared 35 to 40 per cent caustic soda solution. The heat of solution of the alkali raises the temperature to 60 to 80 degrees and enables the reaction to progress rapidly. Hydrogen by this method costs about 20 cents per cubic meter.†

By the **Hydrik** process aluminum powder is acted on by caustic soda giving hydrogen and sodium aluminate, according to the equation,

$$2\,Al + 6\,NaOH = 2\,Al(ONa)_3 + 3\,H_2.$$

Fig. 83 shows a gas generator for the Hydrik process with an hourly capacity of 10 cubic meters.

By the addition of lime, or calcium compounds that form lime, according to ‡ **Consortium für Elektro-chem. Ind. ges. m. b. H.,** nearly the full theoretical quantity of hydrogen is rapidly liberated on heating silicon in an aqueous solution of caustic alkali. The process may be carried out in an iron generator fitted with stirrers, and in British Patent 11,640, May 13, 1911, it is stated that the temperature necessary for the generation of hydrogen from silicon and caustic alkali solutions may be obtained by the solution of the powdered alkali or alkali oxides in water, or by the heat produced in the chemical reaction between aluminium or aluminium alloys and the alkali.

* Met. and Chem. Eng. (1911), 157.

† See Zeitsch. f. angew. Chem. (1912), 2405.

‡ British Patent 21,032, Sept. 14, 1909.

Jaubert (French Patent 430,302, Aug. 6, 1910) uses a strong solution of a caustic alkali, or a solution of sodium or potassium sulfate containing such, which is made to act upon a compound or alloy of silicon (preferably ferrosilicon, manganosilicon or silicospiegel) in such a way, that the heat produced in preparing the alkali solution is utilized in effecting the reaction, no external heat being required. The reaction takes place in a generating vessel, fitted with a stirring device and surmounted by a feeding hopper containing the powdered alloy; this vessel communicates both with an arrangement for washing and cooling the gas and with another vessel, also provided with a stirrer, in which the solution of caustic alkali is prepared (e.g., by dissolving 1 part by weight of sodium hydroxide in 1½ to 2 parts of water). The

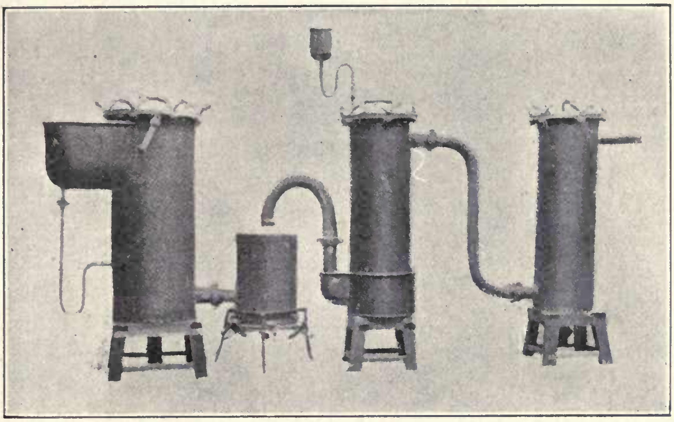


FIG. 83.

water which has served to cool the gas in the condenser passes either to the generator or to the dissolving vessel. A strong solution of alkali being used, an acid silicate is obtained; moreover, non-caustic residues, suitable for use in dyeing and bleaching, are obtained.

The preparation of hydrogen under pressure by the wet method is detailed by Jaubert * as follows:

The reaction by which the hydrogen is produced is carried out under a pressure above the vapor pressure of water at the temperature in question, the larger part of the heat produced is localized and stored in the reacting liquid, and by preventing the vaporization of this liquid, dry hydrogen is obtained, the speed of manufacture is increased, and the amount of liquid necessary for the reaction diminished. The pressure is produced automatically by working with an autoclave generator, in which the hydrogen produced is allowed to accumulate. The generator is a revolving cylinder, provided with an autoclave cover, a charging chamber which penetrates some distance into the interior of the cylinder and a blow-off cock, so that complete mixing of the reagents can be prevented before the reaction is started and to allow the hydrogen formed to be drawn off.

To obtain a rapid and constant evolution of hydrogen by the interaction of silicon, aluminium or alloys containing the same, with an alkali hydroxide, Jaubert (French Patent 454,616, April 30, 1912) prepares an emulsion of a concentrated

* French Patent 433,400, Oct. 25, 1910.

solution of the latter with a non-saponifiable oil or grease, such as paraffin, which mixture is heated to 100° C., with the elements or alloys named, in the form of fine powder, water being added as fast as it is decomposed, and the frothy mass being kept constantly agitated.*

Mauricheau-Beaupre † adds to fine aluminium filings a small proportion of mercuric chloride and potassium cyanide, which causes a slight rise of temperature and produces a coarse powder, quite stable if kept from moisture. This powder is treated with water (about 1 liter to a kilo) and the rise of temperature which occurs as the hydrogen is evolved is watched, and regulated if necessary by the addition of more water so that the temperature does not rise above 70° C. At this temperature 1 kilo of the powder is completely oxidized in about two hours.

The advantages of this method are that the apparatus needed is of the simplest description, and can be made of almost any materials, as the products are perfectly neutral; that the gas produced is pure; and that a very large volume is yielded by a small weight of volume of the reagent (1 kilo yields 1300 liters, or 1 cubic decimeter 1770 liters). Pure aluminium filings with 1 to 2 per cent of mercuric chloride and 0.5 to 1 per cent of potassium cyanide should be used. (French Patent 392,725, July 27, 1908.) Aluminium hydroxide is obtained as a by-product.

Chem. Fabr. Griesheim-Elektron ‡ recommend a preparation consisting of finely-divided aluminium (98 parts) mixed with small quantities of mercuric oxide (1 part) and caustic soda (1 part). On treatment with water, hydrogen is evolved steadily and uniformly, 1 to 1.2 cubic meters (calculated at 0° C. and 760 mm.) being obtained from 1 kilo of the product. The mass can be kept unaltered for a long time if protected from moisture, and can be easily transported, 1 kilo occupying a volume of only 0.8 liter. The cost is about forty-five cents per cubic meter.

In the corresponding British Patent 3188, Feb. 9, 1909, it is stated that aluminium in a divided form, such as filings, dust, chips or factory waste, is mixed with a small quantity of a compound of a metal such as mercury, which is electro-negative to aluminium, and with a small quantity of an alkali or acid, or a borate, phosphate or other soluble substance. The alkali, etc., serves to generate sufficient hydrogen to reduce the mercury or other compound, which then forms an electro-chemical couple with aluminium and decomposes water until the aluminium is used up.

According to **Uyeno**,§ 78 to 98 parts by weight of aluminium are melted in a crucible and a mixture of 15 to 1.5 parts of zinc and 7.0 to

* See also U. S. Patents to Jaubert: 943,022, Dec. 14, 1909; 1,029,064, June 11, 1912; 1,037,919, Sept. 10, 1912; and 1,040,204, Oct. 1, 1912.

† Compt. rend. (1908), **147**, 310.

‡ German Patent 229,162, Jan. 17, 1909.

§ British Patent 11,838, May 18, 1912.

0.5 part of tin are added to the molten metal, after which the alloy is cast in the form of a plate. For each part of this alloy 0.12 to 0.025 part of mercury, or a quantity of zinc or tin amalgam containing this amount of mercury, is taken and amalgamated with the upper and lower surfaces of the plate by rubbing it in with a steel brush. The plate is then heated to as high a temperature as possible without volatilizing the mercury, until the alloy has become uniformly amalgamated, whereupon it is ready for the manufacture of hydrogen by acting on it with hot water.

When zinc dust is heated with hydrated lime, as previously stated, hydrogen is formed according to the equation,

$$CaO_2H_2 + Zn = ZnO + CaO + H_2.$$

On this reaction **Majert** and **Richter** * have based a technical process of generating hydrogen, in which they employ apparatus as shown in Fig. 84. A heating chamber *F* carries a series of horizontal tubes

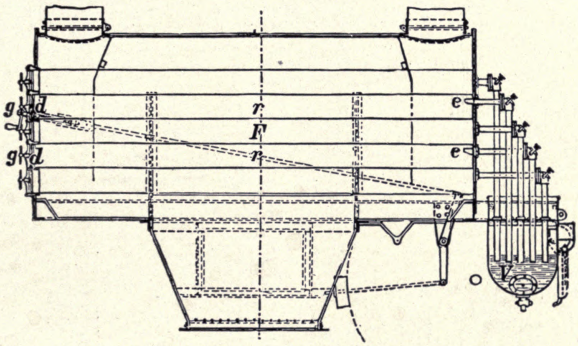


FIG. 84.

r, each of which is provided at one end with a gas eduction pipe *e*, leading to a water seal *V*, and at the other end with a removable cap. Iron or carbon may be used in place of zinc.

In the **Lahousse** process † coal, mixed with barium sulfate, is heated at a red heat so as to produce carbon monoxide and barium sulfide, according to the equation,

$$BaSO_4 + 4\,C = BaS + 4\,CO.$$

The sulfide of barium produced is then heated to redness in a current of steam, with re-formation of barium sulfate and evolution of hydrogen.

$$BaS + 4\,H_2O = BaSO_4 + 4\,H_2.$$

* Brahmer, Chemie de Gase, 101.

† French Patent 361,866, Oct. 24, 1905.

The regenerated barium sulfate is ready for use de novo. The carbon monoxide produced in the first operation may be employed for heating the retorts. Lahousse also states that sulfate and sulfide of strontium may be used in place of the corresponding barium compounds.*

The **Bergius** process. Steam acts on incandescent carbon to produce hydrogen and carbon monoxide. Below 650° C. carbon dioxide instead of carbon monoxide is formed to some extent according to the reaction,

$$C + 2\,H_2O = CO_2 + 2\,H_2.$$

Bergius has found that this reaction occurs almost exclusively if water at a temperature of about 300° C. is allowed to act on carbon under a pressure sufficient to keep the water in a liquid state. The addition of small amounts of thallium salts is beneficial as the reaction is thereby promoted through catalytic action. In order

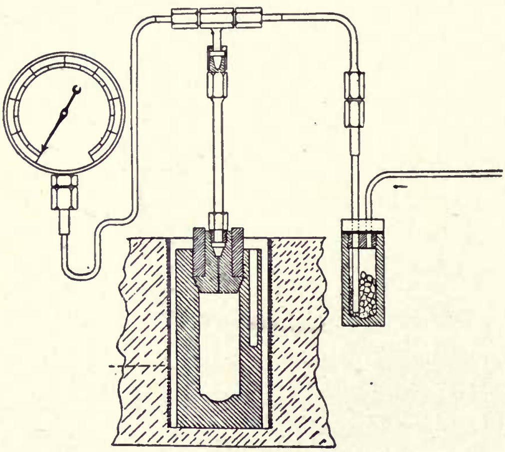


FIG. 85.

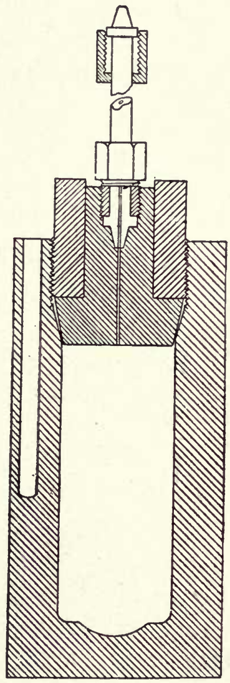


FIG. 86.

to work under the high pressures necessitated by these considerations Bergius has made use of apparatus as shown in Figs. 85 and 86.

The successful closure of the reaction chamber was attained by the use of a tapered plug forced into a seat having a taper of different angle so that the contact becomes a line rather than a surface. (Bergius, Die Anwendung hoher Drucke bei Chemischen Vorgangen, Halle, 1913, 6.) A charge of say 100 kilos coke and 200

* First Addition, Oct. 28, 1905, to French Patent 361,866.

kilos water containing in solution 1 kilo of thallium chloride is placed in a strong iron vessel provided with a valve, and the vessel is heated to 340° C. (German Patent 259,030, June 24, 1911.) The mixture of hydrogen and carbon dioxide which collects in the upper part of the vessel is blown off through the valve at intervals of half an hour, and the carbon dioxide is absorbed by lime.

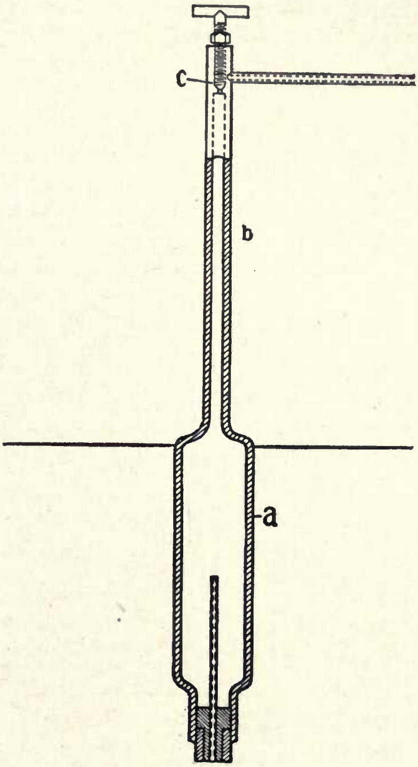


FIG. 87.

Using iron instead of carbon, Bergius * has developed a process of making hydrogen without the accompanying formation of carbon dioxide, based on the reaction between iron or other metal and water at a temperature of 300° C., or so.† A receptacle as shown in Fig. 87 is employed. This has an expanded basal part serving as a reaction chamber and a long tubular outlet.‡

Iron and water (which should contain an electrolyte such as sodium chloride) are placed in the chamber and are heated to 300° C. The pressure rises to 100 atmospheres or higher. Water condenses in the tubular outlet and flows back into the reaction zone. Hydrogen is blown off by means of the valve in the upper part. It is stated that in this way hydrogen can be obtained directly

* Bergius (Zeitsch. f. angew. Chem. (1913), 517) states that with his process hydrogen containing less than 1/100 of a per cent of impurities may be produced. In apparatus which has been thoroughly tested at Hanover, a vessel of a capacity of 80 liters produced 12 cubic meters of hydrogen hourly. Bergius states that the construction of vessels of larger size up to a capacity of about one cubic meter offers no difficulty. In large plants which are arranged for proper heat utilization, Bergius estimates the cost of hydrogen at about 2 cents per cubic meter. The advantage of this process is that very pure hydrogen under high pressure may be produced at a low cost and without an expensive equipment, enabling works requiring only a small amount of hydrogen to produce this gas on the spot at low cost. The iron oxide formed by the reaction can be reduced by heating with carbon at 1000° C. and is then ready to be used a second time.

† German Patent 254,593, Oct. 24, 1911, and German Patent 262,831, July 7, 1912.

‡ Apparatus fitted with an agitator and adapted for the treatment of liquids with gas under high pressures is described in Chem. Ztg. (1913), 1288.

under a pressure of more than 100 atmospheres. Lower oxides of metals may replace the metals themselves. (French Patent 447,080, Aug. 9, 1912.) The water may contain neutral salts, acids or other conductive compounds. The reaction is also accelerated by the use of a second metal, such as copper, nickel or platinum, more electropositive than the principal metal.*

* Badische Anilin und Soda Fabrik., French Patent 441,695, March 23, 1912. Operations in which hydrogen, or gases containing it, are employed under pressure and at a high temperature can be carried out in vessels, provided with special strengthening appliances, although the wall of the interior vessel in which the reaction takes place is composed of some material, such as iron free from carbon or nickel, which is incapable of offering by itself sufficient mechanical resistance to the conditions imposed by the process, but chemically is as resistant as possible to hydrogen. (See also U. S. Patent 1,077,034, Oct. 28, 1913; and 1,075,085, Oct. 7, 1913.)

Hydrogen under pressure may be used in conjunction with vessels constructed of steel alloys at temperatures considerably above 450° C. when these alloys contain certain proportions of chromium, vanadium, tungsten, molybdenum or the like. Suitable alloys contain (1) tungsten 18 and chromium 3 per cent, and (2) chromium 2.9 and carbon 0.2 per cent. Alloys containing too high a percentage of nickel should be avoided. (J. S. C. I. (1913), 1010; Badische Anilin und Soda Fabrik., British Patent 29,260 and 13,258, Dec. 19, 1912, and June 7, 1913.)

CHAPTER XIX

HYDROGEN BY THE ELECTROLYSIS OF WATER

The production of hydrogen and oxygen by the electrolysis of water, though one of the oldest electrochemical experiments, and proposed in a large number of patents, in the past has been carried out industrially only to a limited extent. There was considerable difficulty in developing the laboratory apparatus so that it would operate successfully in practice, one of the hardest conditions to meet being the necessity of absolute safety of operation, and this required the exclusion of every possibility of the formation of an explosive gas mixture. Another difficult matter was the requirement of providing a material for the electrodes, which was not at all or only slightly attacked by the electrolyte, and the necessity of constructing apparatus with a small internal resistance.*

These problems appear now to have been worked out satisfactorily so that large scale electrolysis of water is on a solid industrial basis. The principal processes or systems used in practice include those of the International Oxygen Co., Garuti, Schoop, Siemens-Halske, Schmidt, Schuckert and Burdett.†

* The Electrolysis of Water, Richards and Landis, Trans. Am. Electrochem. Soc., III, 104, and IV, 112, is concerned largely with the theory of the subject, while a paper by Richards bearing the same title, appearing in the Journal of the Franklin Institute, 1905, 377, treats of practical developments in hydrogen and oxygen generation.

† In the electrolysis of water there are certain constants whose values are the same under all conditions of operation within certain limits. The *first* constant is the amount of hydrogen liberated per ampere hour of current passed through the cell generator; the figure is 0.03738 gram or 0.014825 cubic foot of hydrogen gas measured at 0 degree and 760 mm. pressure. Thus, at 400 amperes, which is the customary operating amperage for most cell generators, the production will be 5.93 cubic feet of hydrogen and 2.96 cubic feet of oxygen (at 0 degree and 760 mm. pressure) per hour. At 20 degrees and 760 mm. pressure the output will be 6.36 cubic feet of hydrogen and 3.16 cubic feet of oxygen per hour per cell generator. The *second* constant is the minimum voltage that will force the current through the cell generators. For a solution of sodium hydroxide in water the minimum voltage is 1.69 volts, for potassium hydroxide 1.67 volts; this, then, is the lowest voltage at which decomposition of water, or electrolysis, takes place. In order to produce gas with current at this voltage, the cell generator would have to be constructed in such a manner as to do away with all internal electrical resistance which is obviously impossible and so the operative or practical voltage is higher than the theoretical. With a current of 400 amperes the voltage will vary from 1.9 to 4, depending

D'Arsonval, in 1885, was perhaps the first to install a plant for furnishing oxygen electrically in the laboratory. He used 30 per cent caustic soda solution as electrolyte, cylindrical sheet-iron electrodes, a current density of two amperes per square decimeter, and enclosed the anode in a woolen bag, to serve as a diaphragm. Only the oxygen was saved. The apparatus used sixty amperes, furnished some 100 to 150 liters of oxygen daily, and was in use several years.

Latchinoff used an asbestos cloth partition, ten per cent caustic soda solution, iron electrodes, 3.5 amperes per square decimeter and 2.5 volts working tension; or with a five to fifteen per cent sulfuric acid solution he used lead anodes and carbon cathodes. In his first apparatus, Figs. 88 and 89, the units were all in parallel, but afterwards he used series electrodes, the one side of an electrode acting as an anode and the other as a cathode; a series of forty was

on the type of cell generator. With the first constant given the amount of hydrogen produced per 400 amperes per hour and the minimum or theoretical voltage given it is a simple matter to determine the yield of gas per kilowatt-hour of electricity used. The theoretical efficiency will be 400 amperes × 1.69 volts or 0.676 kilowatt-hour to produce 6.36 cubic feet of hydrogen. The theoretical yield per kilowatt-hour per cell generator will be 9.408 cubic feet of hydrogen. In practice the yield is from 4.5 to 8.25 cubic feet of hydrogen per kilowatt-hour.

In general, electrolytic plants consist of the following important parts, cell generators for producing the gases, a motor-generator set to deliver a direct current at the proper potential or voltage, gasometers and storage tanks for storing the gas as it is generated and compressors and compressor motors for raising the pressure of the gas to the required point. Stripped of everything but essentials the component parts of all cell generators are: a container tank for holding the solution; one or more positive electrodes, one or more negative electrodes, immersed in the solution; means for separating the electrodes to prevent mixture of gas and means for separately collecting the gas as it is generated. The separating medium is usually a diaphragm and may be of metal, earthenware or cloth. The diaphragm may be a conductor or non-conductor of electricity and if of conductive material it should be insulated from the electrodes. The effect of the diaphragm is to divide the generator into two or more partitions, and the gases as generated will rise to the top of the partition, there to be drawn off by means of pipes which lead to header pipes connecting a line of cell generators, each gas, of course, being drawn off by means of separate pipe lines. The header pipes in turn are connected to a main gas line which leads the gases to their respective gasometers. From the gasometers the gas is drawn off by means of compressors and compressed into storage tanks for use.

The majority of installations require a motor-generator set to obtain the required voltage for operating. The current must be direct. The motor-generator set should be heavily built in order to operate on a twenty-four hour load. The compressors employed are specially adapted for handling these gases. The size and character of the gasometers used, of course, depends on the size of the installation.

Below is given a typical operating cost of an electrolytic plant consisting of 100 cell generators with a production capacity of 632 cubic feet of hydrogen and 316 cubic feet of oxygen in one hour and 15,168 cubic feet of hydrogen and 7584 cubic

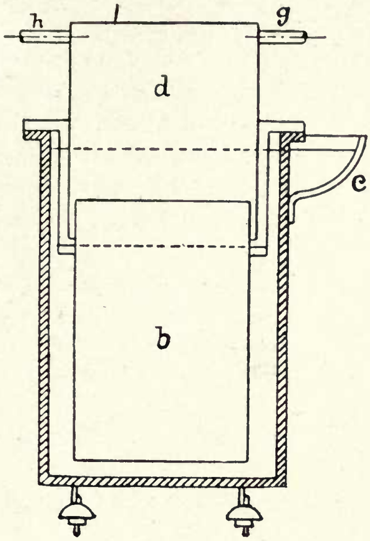


FIG. 88.

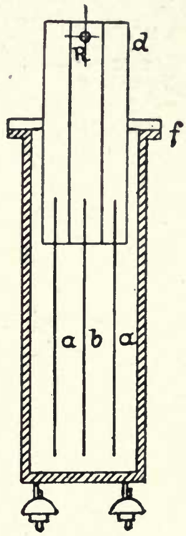


FIG. 89.

feet of oxygen in 24 hours. The yearly production, 300 days 24 hours per day, is 4,550,400 cubic feet of hydrogen and 2,275,200 cubic feet of oxygen.

Each cell generator requires about 2 volts at 400 amperes equivalent to 800 watts or 0.8 kilowatt-hour.

100 cells × 0.8 K.W.H. × 24 hours × 300 days = 576,000 K.W.H. yearly plus 25 per cent for loss through motor-generator set = 720,000 K.W.H. yearly.

Hydrogen compression requires 4 K.W.H. per hour.

4 K.W.H. × 24 hours × 300 days = 28,800 K.W.H. yearly.

(Compression to 300 pounds per square inch.)

Oxygen compression requires 12 K.W.H. per hour.

12 K.W.H. × 24 hours × 300 days = 86,400 K.W.H. yearly.

(Compression to 1800 pounds per square inch.)

Current consumption yearly:	
Cell generators	720,000
Hydrogen compression	28,800
Oxygen compression	86,400
Total	835,200
Fixed charges:	
Depreciation, maintenance, yearly	$3000.00
Interest on investment	1500.00
Labor:	
300 days, 24 hours, at 30 cents per hour	$2160.00

With current at a price of say 1 cent per kw.-hour, which although a low rate is not excessively low for this class of service, the total operating cost will be $15,012.00 per year.

The demand for oxygen in metal working lines is at present so great and so poorly met that in the majority of cases the oxygen produced by an electrolytic plant may be disposed of under contract at such terms as will result in the hydrogen being produced at a relatively low cost.

used on a normal lighting circuit, with current density of ten amperes per square decimeter, and parchment partitions between the electrodes to separate the gases. Latchinoff was also the first to carry out the decomposition under pressure, using a strong iron vessel as electrolyzer, and by an ingenious system of floating valves keeping the pressure of the two gases equal in the apparatus. Fig. 90 shows this apparatus, the action of which will be evident from a short inspection.

Renard's apparatus for the generation of hydrogen is shown in Fig. 91. The container is made of cast iron and serves as the nega-

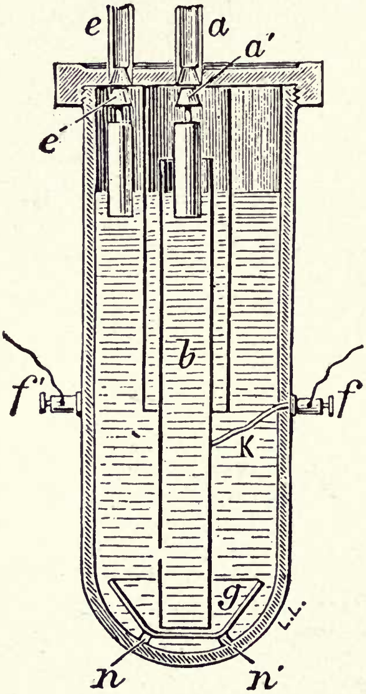


Fig. 90.

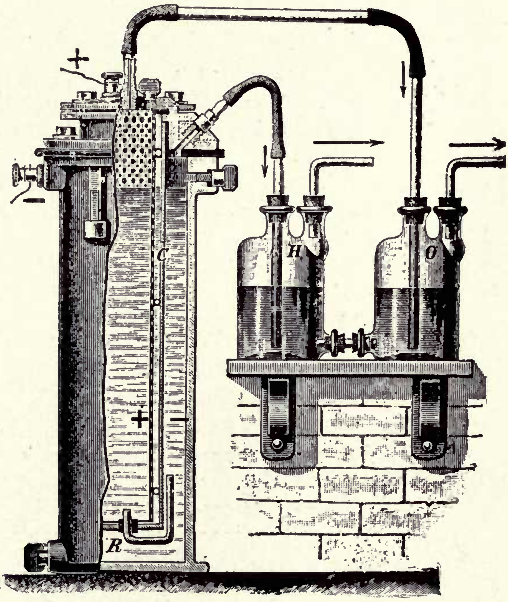


Fig. 91.

tive electrode. The cylinder *C* of asbestos material encloses the positive electrode which is cylindrical in shape and is made either of iron or nickel. Through the bottom of the diaphragm cylinder the U-tube *R* establishes communication between the inner and outer vessels. The electrolyte is a solution made by dissolving 15 parts

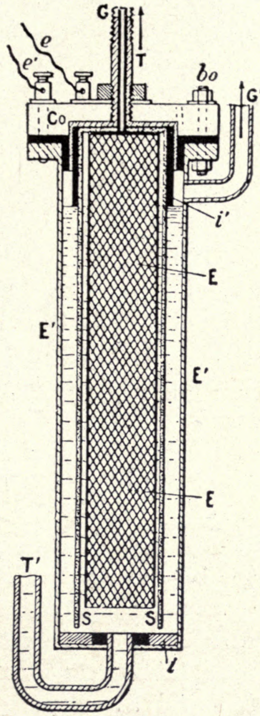


FIG. 92.

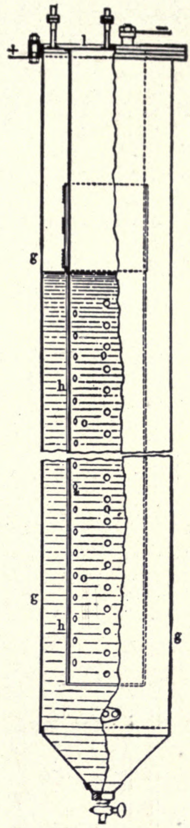


FIG. 93.

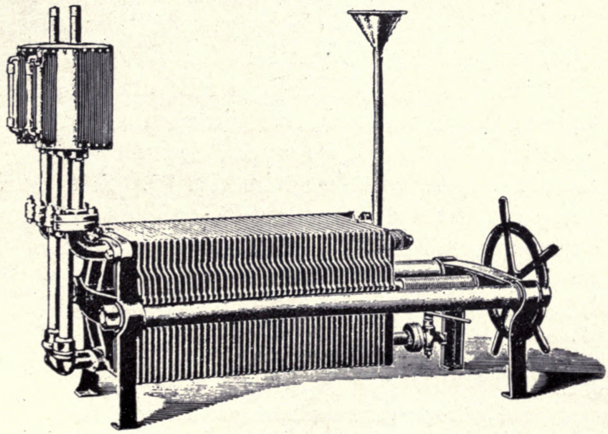


FIG. 94.

of caustic soda in 100 parts of water. Before the gases are passed to the gas holder they are led through the pressure equalizer marked *H* and *O*. With a current of 25 amperes at 3.5 volts a yield of 12 liters of hydrogen and 6 liters of oxygen per hour is obtained.

A form of construction of the Renard * type is shown in Fig. 92 and also in Fig. 93.

The multiple cell of **Schmidt** † looks somewhat like a filter press, Fig. 94, and consists essentially of bipolar, iron electrodes, connected in series. Each frame in the press contains an iron electrode, which acts as a double-pole (bipolar) electrode, sheets of asbestos cloth held between the frames acting as partitions, reinforced with rubber on the edges for making tight joints. The electrolyte is a ten per cent solution of potassium carbonate, filled into the apparatus through the standpipe on the right, which communicates with all the compartments through holes in the frames similar to the usual filter-press construction. The gases evolved escape by similar passages into the cylinders on the left end, where they separate from the electrolyte and pass upwards, while the electrolyte, dragged by the gas bubbles, flows downwards back into the apparatus, thus maintaining an efficient circulation. With forty plates about 2.5 volts are absorbed in each cell, using a current density of about two amperes per square decimeter.‡

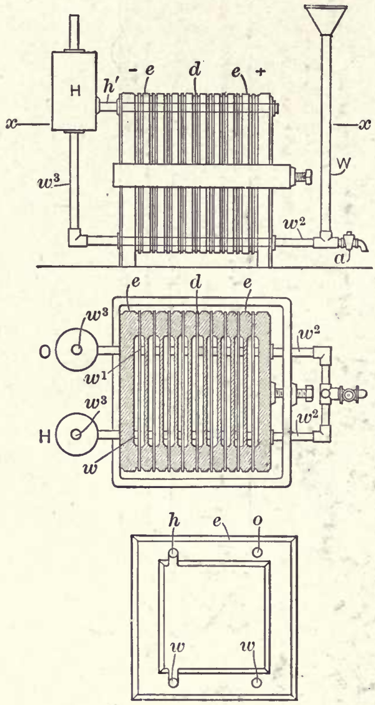


Fig. 95.

The apparatus is shown in detail in Fig. 95. A 110-volt direct-current lighting circuit may be employed for the operation of a series type apparatus composed of the requisite number of cells. The press

* Delmard, German Patent 58,282, Nov. 23, 1890.

† German Patent 111,131, June 13, 1899.

‡ A multiple-cell generator of the filter press type is manufactured by Shriver & Co., Harrison, N. J.

A filter-press type of hydrogen generator having an output of 16 cu. m. of hydrogen per hour is made by Maschinenfabrik Sürth, G.m.b.h. Sürth am Rhein bei Köln.

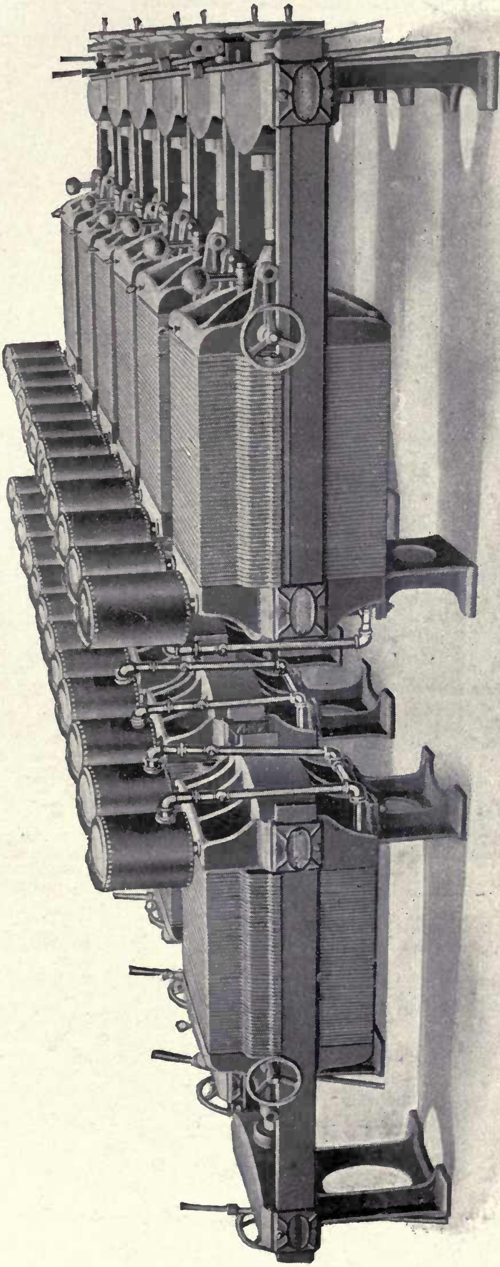


Fig. 96. Shriver oxy-hydrogen generator.

has to be taken apart and cleaned every six weeks and the asbestos diaphragms have to be renewed from time to time.

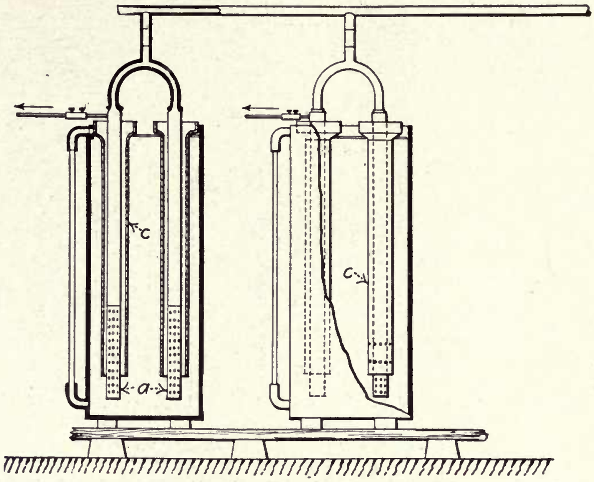


Fig. 97.

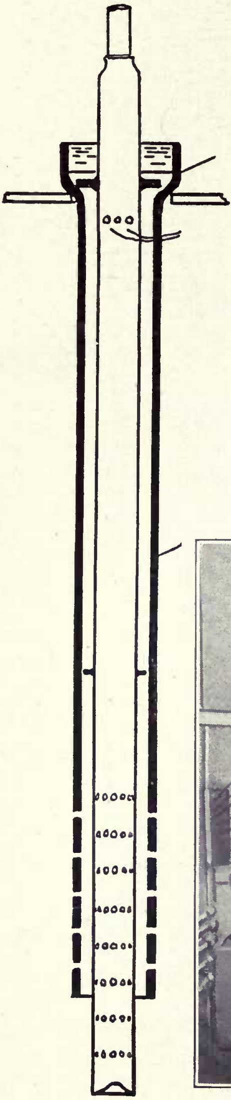


Fig. 98.

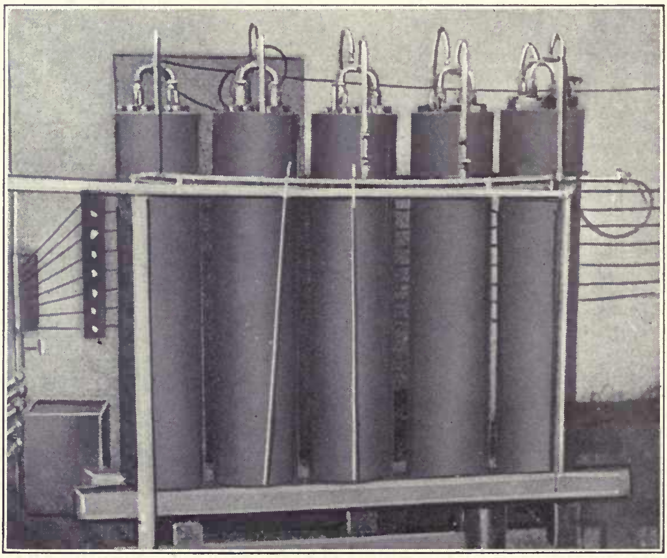


Fig. 99.

Schoop, in 1900, devised an apparatus with non-conducting and non-porous partitions, which has gone into considerable commercial use. Fig. 97 shows the section of the apparatus, where *aa* are the

tubular electrodes of sheet hard lead, enclosed by glass or clay suspended tubes *c*, which are perforated at their lower end; the electrode surface is further increased by fine hard lead or iron wires hung inside the tubular electrodes, the latter being perforated above the level of the electrolyte in order to let the internally-generated gas escape. Each cylinder contains two anodes and two cathodes. When alkaline electrolytes are used and iron electrodes, the working voltage is 2.25; when sulfuric acid of density 1.235 is used, with hard-lead electrodes, the working voltage is 3.6 to 3.9. Fig. 98 shows a single electrode and Fig. 99 an installation of the Schoop system.*

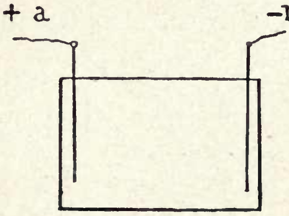


FIG. 100.

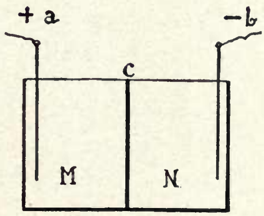


FIG. 101.

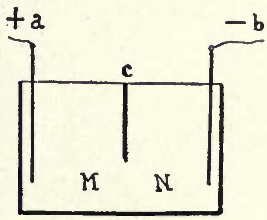


FIG. 102.

Garuti, in 1892, introduced a new electrolytic principle into these apparatus for the decomposition of water. He used a nearly complete metallic partition between the electrodes, and avoided the evolution of gases on this partition by keeping the working voltage between the electrodes below three volts. A metallic partition can only act as an intermediate or bipolar electrode by virtue of the current entering and leaving it; but this would make two decompositions between

* Schoop (Zeits. Elektrotechn. Wien (1900), 18, 441) discusses the difficulties met with in the construction of a suitable apparatus for the technical electrolytic manufacture of hydrogen and oxygen, and gives a description of patents dealing with this subject. In the Schoop apparatus it is claimed that 1.5 cubic meters of hydrogen and oxygen are produced per 11 horse-power hours. Richards (Jour. Franklin Inst. (1905), 390) notes that the output is given as 68 liters of oxygen and 136 liters of hydrogen per electrical horse-power hour. A description of the Schoop system is given in the Centralblatt f. Accum., Feb. 15, 1903. It is stated that the length of the tubes is chosen according to the pressure under which the gases are wanted. The following results were obtained with the Schoop apparatus during one year: One electric horse-power hour gives 97.5 liters of hydrogen and 48.75 oxygen (probably under atmospheric pressure); i.e., for one cubic meter of mixed gas 6.8 horse-power hours are required; with warm acid (sulfuric acid of 1.23 specific gravity being always used) this value is reduced to 6.2 horse-power hours; if the price of one horse-power is 1 cent, the cost of the production of one cubic meter of mixed gases is 4.2 to 4.8 cents. The purity of the oxygen is 99 per cent, that of the hydrogen 97.5 to 98 per cent.

the original electrodes, necessitating an absorption of $2 \times 1.5 = 3$ volts in decomposition. As long as the working voltage is kept below 3, the partition must act merely as a partition, the same as a non-conducting partition. Reference to Figs. 100, 101 and 102 will make this entirely clear. If 2 electrodes are placed in a vessel (Fig. 100) containing acidulated water and are separated by a sheet of metal *c* (Fig. 101), two separate decomposition chambers result and the sheet metal serves as a bipolar electrode, so that the side towards the anode evolves hydrogen and that towards the cathode, oxygen. Since the 1.5 volts are required for the decomposition of water, the cells *M* and *N* will require 3 volts. If the diaphragm is raised somewhat so the chambers *M* and *N* are in communication (Fig. 102) the evolution of gas will take place only on the terminal electrodes and not on the intermediate conducting septum. The latter becomes a bipolar electrode only when the electromotive force exceeds 3 volts. The advantage gained by the Garuti process is in the simplicity and economy of making the partitions of sheet metal instead of burnt clay, rubber, glass, etc.

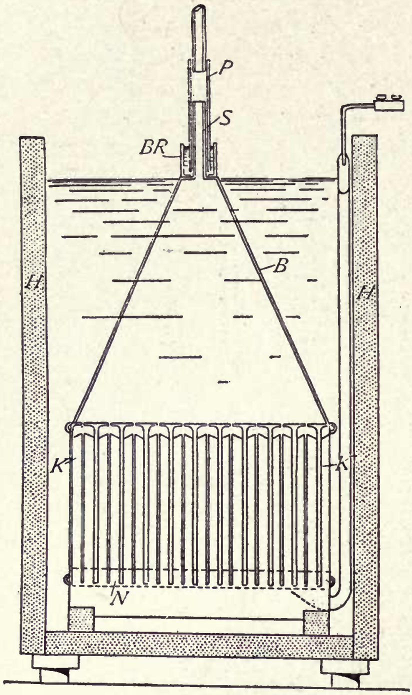


Fig. 103.

Garuti devised many modifications in the details of his cells, of which Fig. 103 may represent the most recent. The original forms made of sheet lead (using dilute sulfuric acid electrolyte) got out of shape too easily, and were replaced by sheet-iron apparatus, using caustic soda solution. The electrodes are only twelve millimeters from each other, and separated by a sheet-iron partition with small perforations in it, the latter allowing free passage of current but being too small to allow any gas bubbles to pass. The alternate compartments are connected with oxygen and hydrogen mains, in which are enlargements for collection of spray and moisture, which runs back into the cell. Current densities of two to three amperes per square decimeter are possible with a working voltage between 2.45 and 3,

using caustic soda solution of 21° Bé. The cell shown in Fig. 104 is intended to take 400 amperes, and to require one kilowatt of power.

The Garuti type C11 generator consists of 45 separate compart-

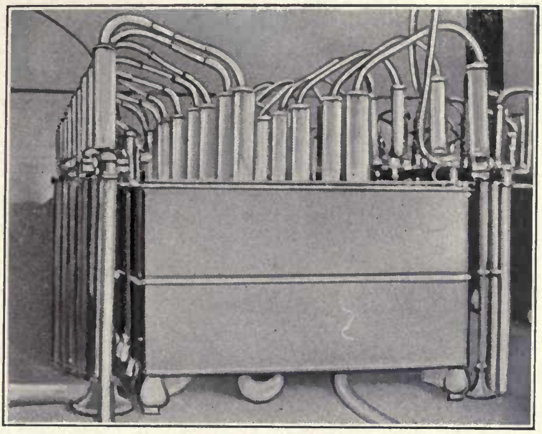


Fig. 104.

ments made of 16-gauge sheet iron welded together to form a single unit.* The sides of the compartments are used as diaphragms and are usually perforated (Fig. 105) to allow circulation of the electrolyte but

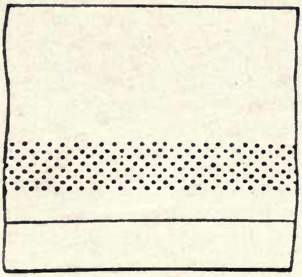


Fig. 105.

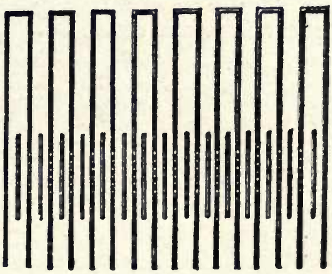


Fig. 106.

Perforated compartment walls of the Garuti generator.

* In 1892 Garuti took out a patent (British Patent 16,588, April 25, 1892) describing an apparatus consisting of a container having an inverted leaden case with partitions of sheet lead soldered together so as to form a case divided into parallel cells open only to the water at the bottom. The partitions of the cells separate the anodes and cathodes which are placed alternately and are insulated in the cells by means of combs made of suitable material. In 1896 Garuti and Pompili (British Patent 23,663, Oct. 24, 1896) described an improvement on the former patent, involving the perforation of the diaphragms in their lower part by small holes as near as possible to each other. See also U. S. Patents to Garuti 534,259, Feb. 19, 1895, and Garuti and Pompili 629,070, July 18, 1899.

not the gas. The perforations extend lengthwise along the lower edge of each compartment wall 3 inches from the bottom, forming a perforate strip $2\frac{1}{2}$ inches wide. An electrode is placed in each compartment and the electrodes are alternately positive and negative. All like electrodes are connected together. Each compartment is $\frac{3}{4}$ inch in width and 30 inches long. The electrodes are insulated from the compartments and are prevented from coming in contact with the walls by means of small porcelain insulators. The gas from all of the hydrogen-producing compartments is collected in a gas bell welded to one side of the cell proper and is led through a water seal and to a header pipe and then to a gasometer. The oxygen gas is handled in a like manner. The cells as well as the container tanks and pipe lines are insulated from the ground. The pipe from the cell to the header pipe is insulated from the latter by means of a sleeve of rubber and glass.*

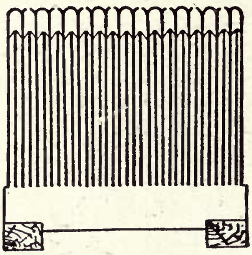


FIG. 107. Compartments of the Garuti generator.

Siemens Bros. & Co. and **Obach** devised the apparatus shown in Fig. 112, the principle being similar to that of the Garuti. The cast-iron vessel *a* is surrounded by heat-retaining material, in order that the temperature of the cell may be automatically raised and thus its running resistance lowered. A cylindrical iron anode *f* is separated from the encircling cathode *g* by a cylinder of wire netting *c*, held in place by the porcelain block *k*. The electrolyte is dilute caustic soda; the gases escape above from the spaces *n* and *m*. The whole

* When the Garuti cell is first installed the efficiency will often be as high as 6 cubic feet or so of hydrogen per kw.-hour, but the depreciation is said to be perhaps more rapid than in some other types of generators and in time the hydrogen output may drop to about 5 cubic feet. Thus under the normal operating amperage of 350 or 400, from $2\frac{1}{2}$ to 3 volts per cell will be required. The rather rapid depreciation of the generator is said to have held back its use to some extent. Owing to the lightness of the materials employed and also possibly because of insufficient electrode surface, the anode is liable to be attacked and eventually worn away. The minute particles of iron or iron compounds formed are said to have a tendency to be deposited on the cathode. The insulators, employed to prevent the contact of electrode with the compartment wall, form a convenient place of deposit for the iron particles with possible danger of causing a short circuit between the electrode and the compartment walls. If one compartment is short circuited the entire cell becomes "shorted" and this short circuit will cause the generation of mixed gas. The entire cell should be dismantled about once a year and cleaned with either a stream of water or by means of a sand blast.

The American Oxhydric Company, Milwaukee, Wis., have had generators of the Garuti type in operation for several years.

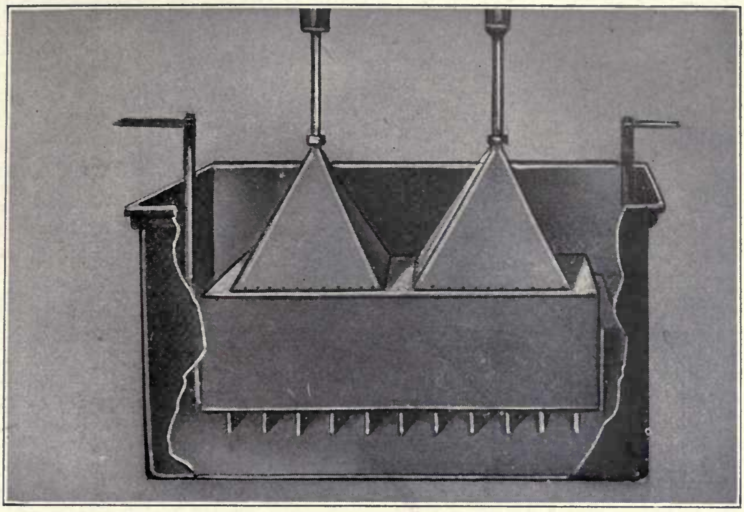


FIG. 108. Garuti generator.

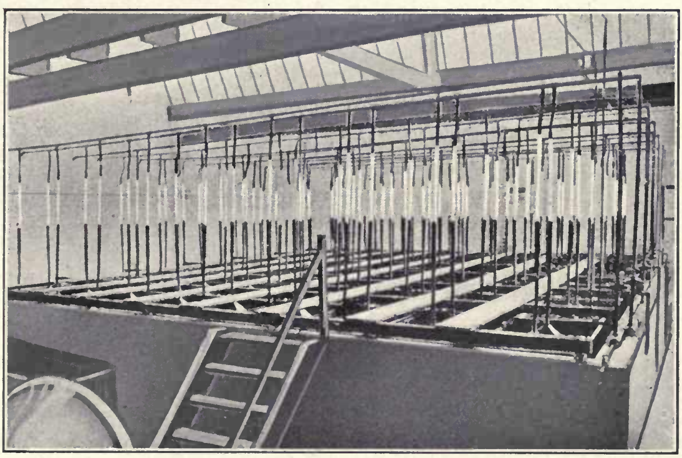


FIG. 109. Battery of Garuti generators.

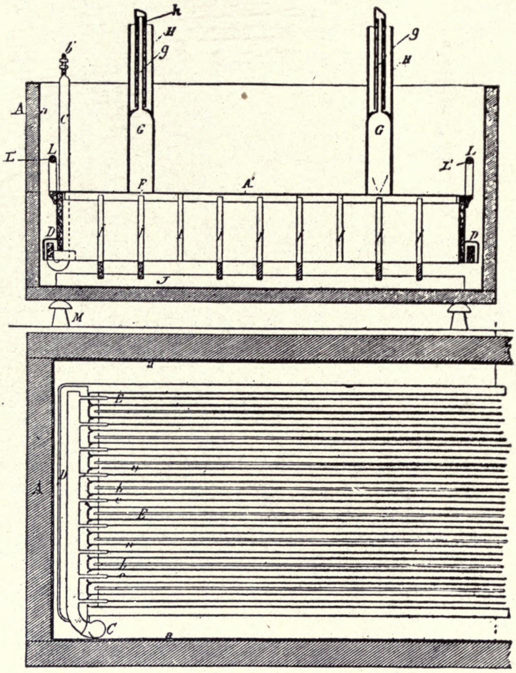


FIG. 110. One form of the Garuti generator.

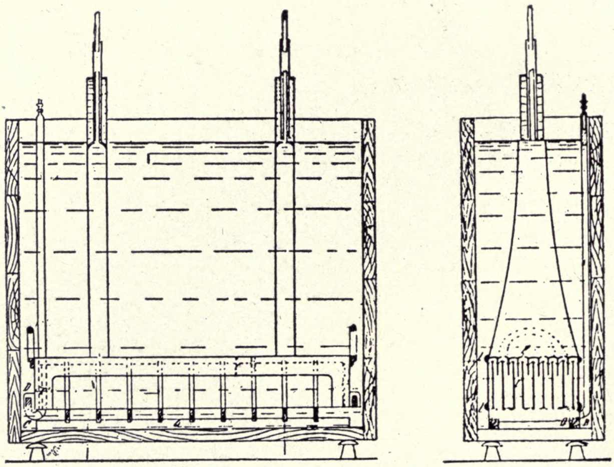


FIG. 111. A modified form of the Garuti generator.

apparatus is set on insulating porcelain feet. The normal type of apparatus is built to take 750 amperes at 3 volts drop of potential, and furnishing eleven cubic meters of oxygen and twenty-two cubic meters of hydrogen per twenty-four hours, using up 162 kilowatt-hours.*

Fiersot describes † an apparatus of Siemens and Halske for the electrolysis of water in which a 10 per cent

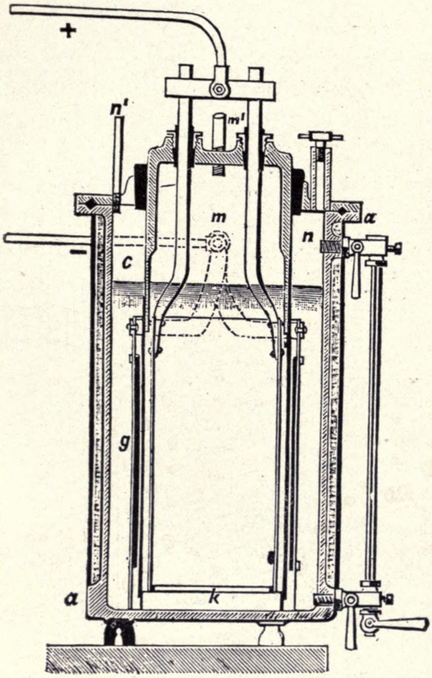


Fig. 112.

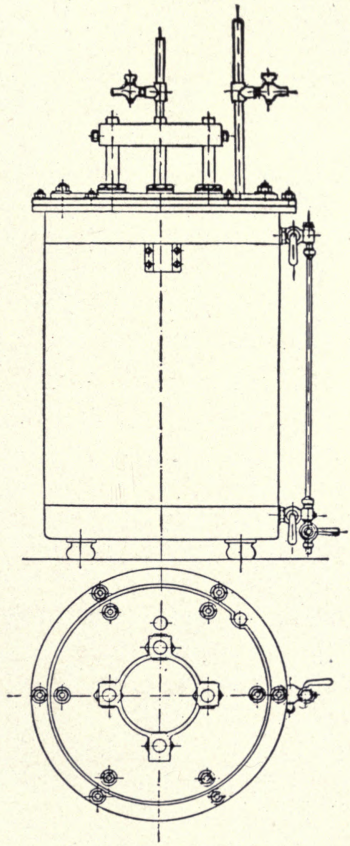


Fig. 113. Plan and elevation of Siemens Bros. and Obach generator.

solution of potassium carbonate is used as electrolyte. One hundred and thirty-four grams of water are decomposed per kilowatt-hour. By heating the electrolyte the output may be increased by 8 per cent. The electrolytic oxygen thus produced is on the average 97 per cent pure, while the hydrogen contains one per cent of oxygen.

Another form of metallic diaphragm cell has been devised by **Fischer, Luening and Collins.**‡ The generator consists of a tank

* Jour. Franklin Inst. (1905), 392.
† Electrochemical Ind. (1904), 28.
‡ U. S. Patent 1,004,249, Sept. 26, 1911.

containing an electrolyte in which an indifferent number of independent, preferably oblong, metallic cases are submerged. An illustration of the case is shown in Fig. 114. The case is open at the bottom and is divided into a pair of cells by a metallic diaphragm. Electrical connections to the anode and cathode and exit pipes situated on the upper side of the case are provided for the removal of the gases.

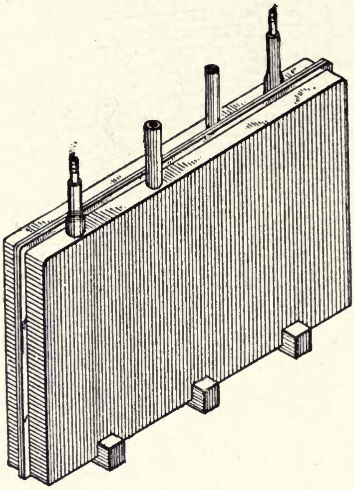


FIG. 114.

The apparatus of the **Schuckert** system * is constructed, with the exception of the copper feed wires and the insulating material, entirely of iron. The cell proper of a unit designed to accommodate 600 amperes consists of a cast-iron trough (Fig. 115), approximately twenty-six inches long by eighteen wide and fourteen deep, requiring, when in operation, about 50 liters of electrolyte. In this trough are placed the iron electrodes. These are separated by strips of a good insulating material, extending from the top downward about three-fourths the depth of the cell. Between these separating plates and enclosing the electrodes are suspended iron bells, which collect and carry off the gas there generated. The electrolyte is usually a 20 per

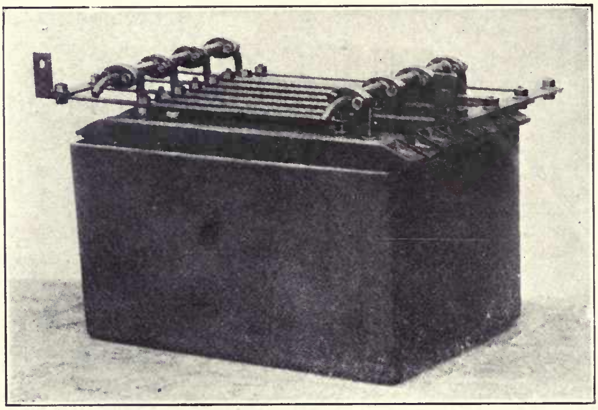


FIG. 115. Schuckert cell.

* Electrochem. Ind. (1903), 579.

cent aqueous solution of pure sodium hydrate, although a 15 per cent solution may be used. The concentration is maintained by supplying to the cells an amount of distilled water equal to that decomposed and carried away mechanically by the gas. The loss of sodium hydrate

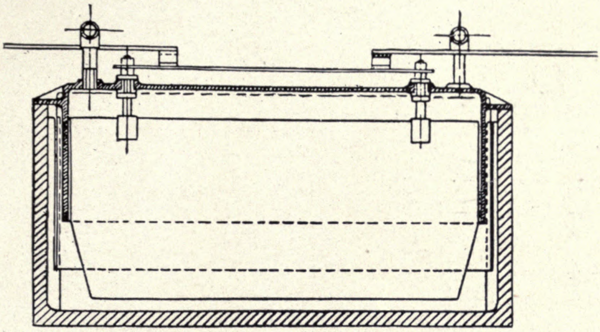


FIG. 116. Longitudinal section of Schuckert cell.

is inappreciable and may be entirely eliminated if the first wash water be used as feed water for the cells. The units may be connected either in series or parallel with a drop of potential between electrodes of from two and one-half and three volts. The apparatus is operated

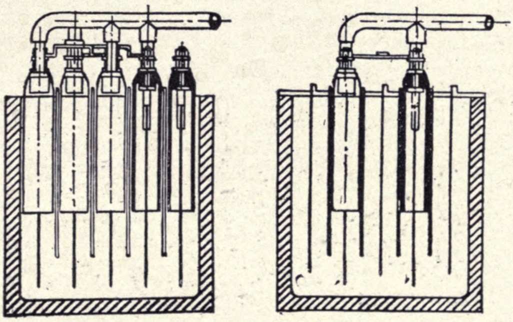


FIG. 117. Cross section of Schuckert cell.

most economically at a temperature of 70° C. When the cells are protected from radiation, as can be done, for example, by placing them on wooden boxes and packing them in one or two inches of sand, the heating effect of the passing current is sufficient.*

* The Elektrizitäts-A-G. Vorm. Schuckert & Co. have taken out German Patent 231,545, Aug. 13, 1910, for the addition of soaps or soap-forming substances, preferably emulsified soaps, and of ferric oxide to the alkaline electrolyte employed.

Fig. 118.

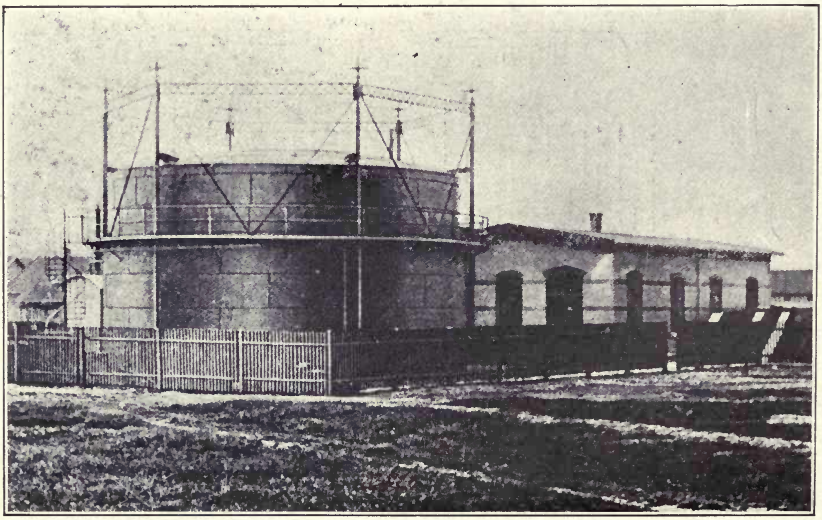


Fig. 119.

The standard types of apparatus are designed to take from 100 to 1000 amperes, and to furnish gas at a pressure equal to a water column of 70 to 80 mm. For special purposes a cell delivering gas sustaining a water column of 760 mm. may be secured. The production of normal types of apparatus is about 150 liters of hydrogen and 75 liters of oxygen per kilowatt-hour when measured over water at atmospheric pressure, and at 20° C. The attention required for a plant of this kind consists simply in supplying the requisite amount of water to maintain the concentration constant. When in continuous operation the positive electrode, which is made up of a sheet iron plate two millimeters thick, should be replaced at the end of each year.*

Fig. 118 shows the interior of a plant furnishing 1200 cubic meters hydrogen daily. Fig. 119 shows the exterior of this plant. An equipment for an hourly production of 4 cubic meters hydrogen is shown in Fig. 120. Fig. 121 is a compression room for charging cylinders with oxygen at 150 atmospheres pressure.

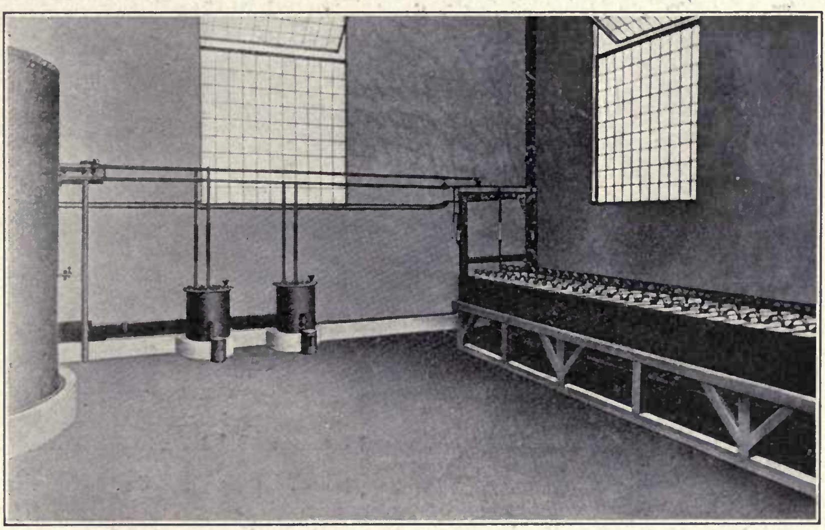


FIG. 120.

A modified form of the Schuckert cell, as shown in Figs. 122 and 123, comprises a container tank, constructed of welded sheet iron and a number of positive and negative electrodes immersed in the solution. Eight separate bell castings are employed to house the electrodes and collect the gas as it is generated. These bell castings are made of a close-texture gray iron and are suspended from the top of the container tank by means of U-shaped steel supports. The container tank and the bell castings

* See Sci. Am. Suppl. (1913), 363.

play no part in the operation of the generator and are insulated from the electrodes and all current-carrying metal. The electrodes are made of steel plates to each of which are welded two steel rods, both rods serving as terminals as well as supports for the electrode, holding it in position within the bell casting. The electrodes are alternately positive and negative. All of the positive electrodes are connected together by means of bus bars across the top of the tank and are led to a common terminal. The negative electrodes likewise are connected together and led to a common terminal. Each bell casting is tapped for an eduction pipe to draw off the gas as generated. The four hydrogen pipes are connected together as shown and are led to the hydrogen pipe line connecting a battery of generators. The oxygen pipes are connected likewise. The electrolyte fills the container and owing to its height above the electrodes the gas is generated under an appreciable pressure amounting to approximately one pound per square inch.

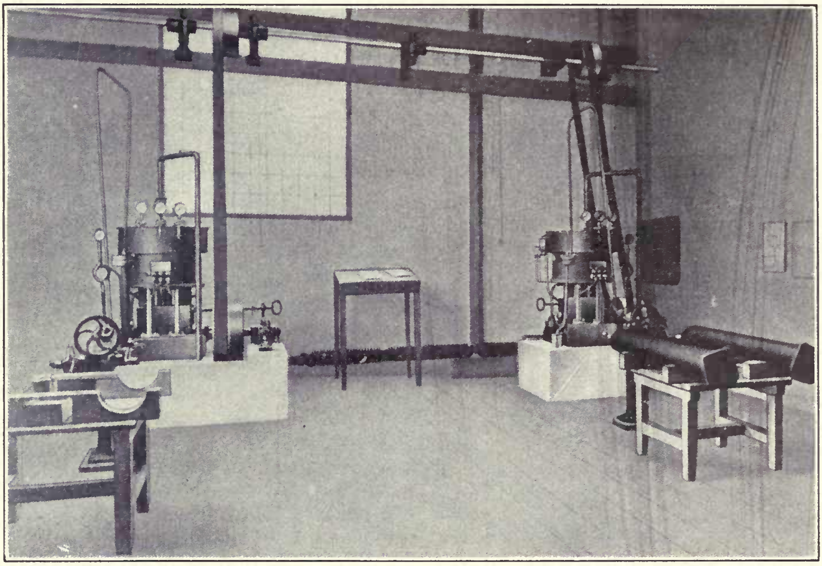


Fig. 121.

The novelty that distinguishes the Schuckert cell from the majority of other generators is the absence of any diaphragm in the construction. While a diaphragm is actually not used, still the sides of the bell castings act in the capacity of a diaphragm to prevent the mixing of the gases.

The working efficiency of the Schuckert cell under normal conditions of temperature is said to average from 4.5 to 5.5 cubic feet of hydrogen per kilowatt-hour of electricity passed through it. Or, in other words, the voltage required to force 400 to 600 amperes through each cell will vary from 2.9 to 3.5 according to the condition of the plant. The Schuckert generator was one of the earliest placed on the market and at the present time three plants of this type are reported in use in the United States. Too high an amperage results in so rapid an evolution of gas that there is

a tendency under these conditions for the gas in one chamber to be forced down and under the wall of the next partition which, of course, will result in mixed gas or the escape of gas into the generator room.

Another difficulty said to be met with in operating under high amperage is the wearing away of the anode, charging the electrolyte with small particles of iron compounds which show a tendency to be attracted to the cathode and gradually form a deposit. These accretions have been known to build across the space between the electrode and the bell castings causing short-circuiting and permitting the bell castings to become charged, with consequent evolution of gas on its outer side and the escape of gas into the generating room.*

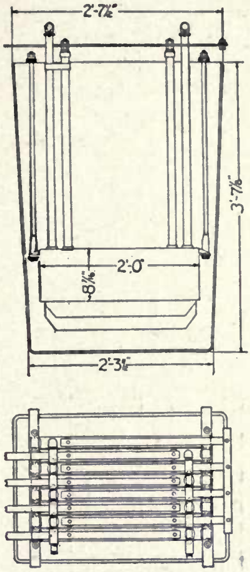


FIG. 122.

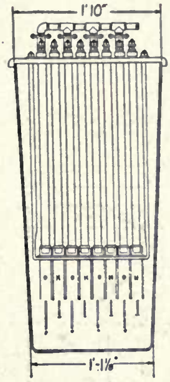


FIG. 123.

Details of construction of an electrolytic apparatus for the production of hydro-

* The Schuckert apparatus is supplied by the Elektrizitäts-A-G. Vorm. Schuckert & Co., Nurnberg. In a private communication they state that an electrolyzer battery, capable, when running at a temperature of 50° to 60° C., of producing hourly 10 cubic meters of hydrogen, yields the gas of 99.5 per cent purity. For this equipment they quote:

Electrolyzer	$2350
Caustic soda (containing a little chlorine and sulfur) 1450 kilos	410
Insulating material	100
2 scrubbers, driers, and safety devices, pressure regulators and gauges	250
2 gas-purifying stoves	500
Packing for over seas and freight	240
Total	$3850

Other auxiliaries are:

2 gas holders (10 and 20 cubic meters)	$2000
Wooden staging and boxes to contain the battery embedded in sand for protection against loss of heat	200
Compressors	2850
Water-distilling apparatus	200
Miscellaneous	525

The temperature of the electrolyzer room should be maintained at least at 15° C. In cold weather it must be heated.

An electrolytic hydrogen and oxygen generator of the bell-collector type is described by Benker (J. S. C. I., 1914, 256, and French Patent 461,981, Aug. 29, 1913).

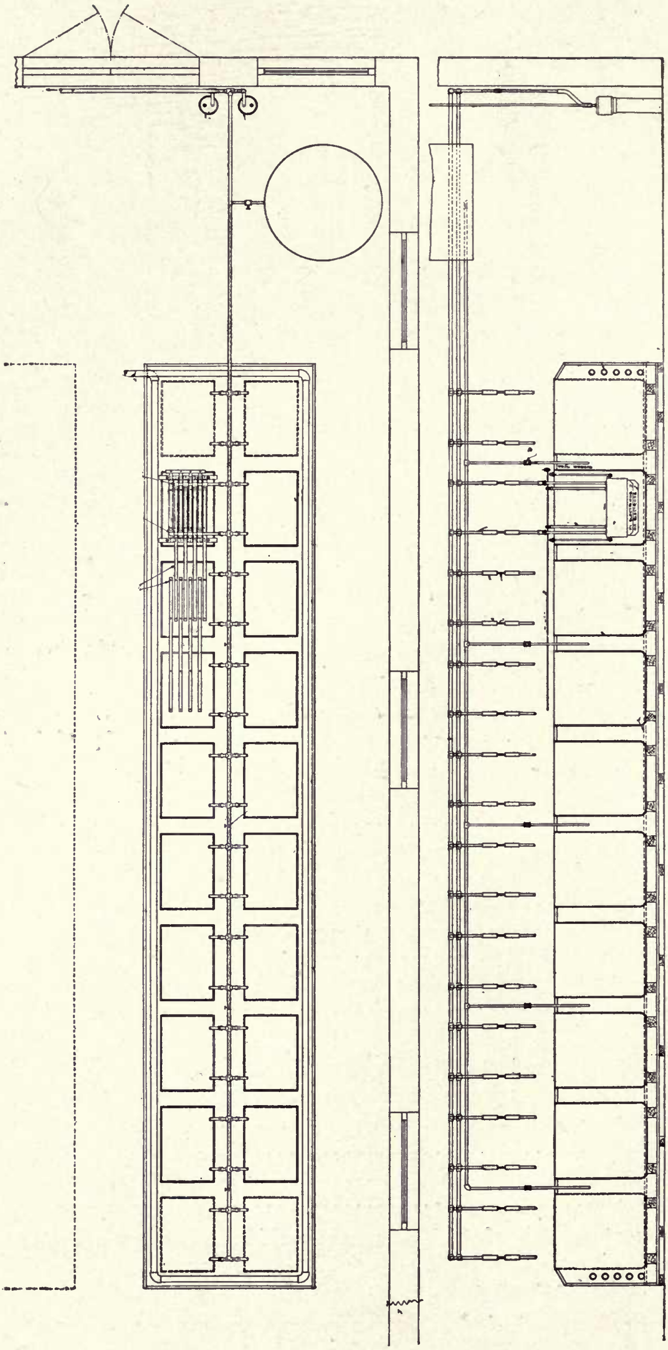


FIG. 124. Oxygen-hydrogen plant. Schuckert type.

gen and oxygen are given by **Van Scoyoc** (U. S. Patent 813,844, Feb. 27, 1906), in which the operation is rendered continuous by the use of automatic float-valves. The level of the acidulated water in the electrolyzer is maintained constant by means of a float-valve in the supply pipe. The two electrodes are placed in two compartments which are open at the bottom. Each compartment is divided into a lower and an upper chamber, connection between the two being made by automatic float-valves. When the pressure of the gases generated in the lower chambers becomes great enough to lower the level of the water, the valve is opened and the gases pass into the other chamber and then into gas bags.

Aigner* charges an alkaline electrolyte into an iron vessel *G*, Fig. 125, in which an iron drum *T* rotates, the outer surface of the latter being amalgamated.

The upper part of *G* is divided into two compartments *R* and R_1 by the partition *S*, which extends downwards nearly to the drum *T*. The oxygen and hydrogen are led off through separate outlets in the cover *D*. The electrolyte is introduced and withdrawn through the opening *L*. At the anode *A* hydroxyl ions are depolarized, with formation of water and gaseous oxygen, the latter escaping into the compartment *R*, while an equivalent quantity of sodium ions is depolarized and combines chemically with amalgam on the surface of the drum adjacent to the anode. When this portion of the drum comes below the cathode *K* hydroxyl ions are depolarized with formation of sodium hydroxide, the sodium being redissolved from amalgam, while sodium ions are depolarized with formation of sodium hydroxide and gaseous hydrogen.

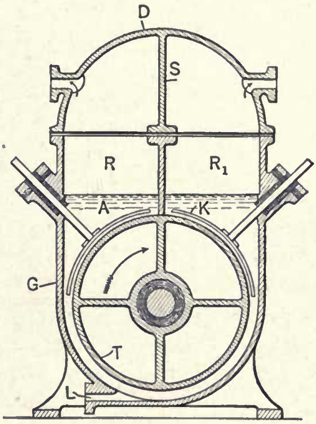


FIG. 125.

The electrodes of the **Cowper-Coles** generator† consist of metallic sheets provided with tongues, which project downwards at an angle of about 45 degrees with the faces of the sheets. These electrodes are placed in separate collecting boxes or chambers, the liberated gases being guided into the latter by the inclined tongues of metal which project within openings in the sides of the chambers. A battery of generators may be enclosed in a water jacket and provided with means for keeping the solution in each cell at a common level.

Dansette (French Patent 391,793, Sept. 6, 1907) has devised an arrangement for feeding water vapor into the zone of an electric arc produced in a gas-tight electric furnace, by passing water through the lower, vertical, carbon tube, which constitutes one of the electrodes. The furnace communicates by means of a valve with a reservoir, into which the hydrogen and oxygen produced by dissociation pass. The oxygen may either be absorbed by a suitable reagent, or the two gases separated by diffusion through a porous earthenware vessel.

* German Patent 198,626, Nov. 13, 1906.

† British Patent 14,285, Dec. 20, 1907.

An electrolyzer for the production of pure hydrogen and oxygen which is suggestive of the Schmidt type has been designed by **Eycken, Leroy** and **Moritz.*** The electrode plates are built up with separating diaphragms of asbestos, in the form of a filter-press. Openings in the top of each plate form two channels for the escape of the gases. The gases are kept at a pressure above that of the atmosphere, rendering the danger of accidental mixing remote. The electrodes and diaphragms are kept clean by making the first electrode hollow, and in the form of a large reservoir, in which the sediment accumulates and from which it may be removed from time to time. This reservoir is divided into two parts, into which the gases pass, through the electrolyte, the pressure being maintained constant, and the delivery of the gases regulated by two floats and balanced valves.

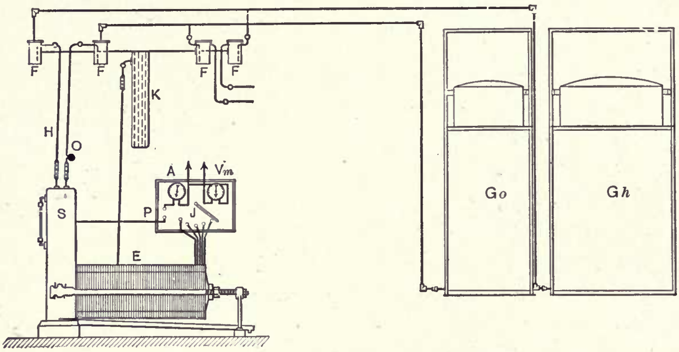


FIG. 126.

Siegfried Barth of Dusseldorf builds "oxhydrogenerators" constructed in accordance with the foregoing system. The parts of the generator are very heavy so that durability is insured. The electrode plates are insulated by extra heavy, almost indestructible, diaphragms. A very powerful circulation of the electrolyte over the surface of the electrode is obtained, resulting in an efficient removal of the gas particles which otherwise would cling to the electrodes for a considerably longer period. Great pains have been taken to guard against mixing of the gases so as to procure pure products. Caustic soda or potash in distilled water is used as the electrolyte. When used uninterruptedly, the cell becomes warm and its output is improved, and for intermittent operation a steam-heating arrangement is attached to the generator so that it may be heated quickly and brought to full capacity without loss of time. The ordinary type of this generator is made to deliver both hydrogen and oxygen under a pressure of about 50 to 80 cubic meters water column, but special forms are furnished which operate under a pressure of about 4 kilos (8 to 9 pounds). A generator having an output of 6.6 cubic meters of hydrogen and 3.3 cubic meters of oxygen per hour, requiring 160 amperes at 250 volts is 4.4 meters

* French Patent 397,319, Dec. 9, 1908.

long, 0.72 meter wide, and 2.05 meters in height, and weights 6600 kilos; the cost being $2175. (Fig. 126.)*

Another apparatus of the filter-press type † is designed especially to produce the gases at relatively high pressure without the purity of the product being affected. Fig. 127 shows a form of electrode plate and Fig. 128 a view of one end of the generator, showing a collecting tower with regulator float and a series of plate electrodes.‡ §

The electrolytic cell of **Tommasini** as shown in Fig. 129 contains vertical anodes 6 and cathodes in the form of inverted U-shaped receptacles 5. The outside of these receptacles 5 is covered with an insulating apron 7 which extends to a point above the liquid line, and to a point below the lower edge of the cathode 5 proper, so that an overhanging apron 8 is provided. The gases evolved at the plates 6 and accumulated in the top of the inverted receptacles 5 are conducted off separately, the hydrogen passing through the pipe 12 into the safety device 14. The height of water is less in the safety device 14 than in the receptacles 5, so that when the pressure of the hydrogen gas becomes so great as to tend to press the fluid out of the chambers 5 (which would result in the mixing of the hydrogen with oxygen) the pressure of the hydrogen gas will first press the water out of the receptacle 19 and pass out of slots 20, so as to relieve the pressure in the receptacles 5. The aprons 8 at the bottom of the compartments 5 also prevent mixing of the two gases.‖

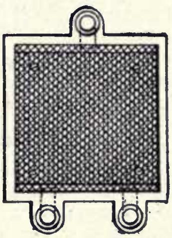


FIG. 127.

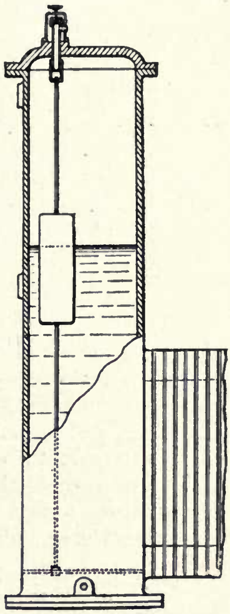


FIG. 128.

* A multiple-cell electrolytic generator has been patented by Levin, U. S. Patent 1,094,728, April 28, 1914, assigned to the International Oxygen Co.

† Moritz, U. S. Patent 981,102, Jan. 10, 1911.

‡ In the generator of L'Oxhydrique Francaise (French Patent 459,967, Sept. 21, 1912, and addition, June 25, 1913), the diaphragm of each element is composed of asbestos fabric, which is nipped between two wooden frames. The latter are bored so as to provide conduits for the evolved gases and the electrolyte. The electrodes are composed of light sheet iron, grooved or corrugated, so as to possess as much active surface as possible. The electrodes may be nickelled on their anode sides. The apparatus comprises a series of such elements.

§ See also U. S. Patent *Reissue* 13,643, Nov. 11, 1913.

‖ U. S. Patent 1,035,060, Aug. 6, 1912.

Buffa (Electrician (1900), 46) states that one of the chief difficulties met with in the electrolysis of water on the large scale is the mixing of the oxygen and hydrogen given off at the two electrodes. If, in order to avoid this mixing, a diaphragm be introduced, the resistance of the cell increases to such an extent that the efficiency of the apparatus is seriously reduced. A better method is to use metallic septa; these separate the two gases perfectly, and act as intermediate electrodes. Since the reduction of voltage, both from the anode to one side of the septum and from the other side of the septum to the cathode, is insufficient to cause decomposition

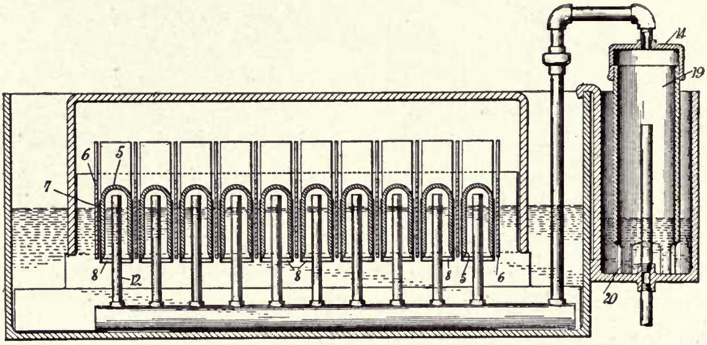


FIG. 129.

of the water, liberation of the products of electrolysis does not occur at either surface of the metallic septum, but is confined to the electrodes proper. In practice, iron electrodes in a 11 per cent solution of caustic soda have been found to be most convenient and economical. The electrolyte is covered with a film of mineral oil, in order to prevent absorption of carbon dioxide from the air. It has been observed that the same protective action is afforded by a film of water vapor, which obtains when the temperature of the electrode is fairly high; when, however, the temperature drops to 10° C. or under, absorption of carbon dioxide takes place rapidly.

With the object of completely preventing admixture of the two gases and at the same time keeping the electrical resistance low, **Vareille** arranges the electrodes as shown in Fig. 130. Vertical rows of V-shaped troughs are provided with suitable insulation and serve to separate the positive and negative electrodes which are placed on opposite sides. The extremities 20 of these troughs are lower than the ends of the electrodes 13, so that the bubbles of gas coming from the latter cannot mix. The electrodes are both insulated from the container.*

In a modification, the troughs, described above, for the separation of the electrodes are replaced by vertical series of elements each of triangular section, and either solid or hollow. Each electrode consists of a sheet, with U-shaped pieces bound on each side with rivets. The gases are collected in bells, either stamped out of sheet metal or consisting of sheets cut out and folded, and united at the angles by autogenous soldering.†

* French Patent 355,652, June 27, 1905, and U. S. Patent 823,650, June 19, 1906.
† First addition, Oct. 28, 1908, to French Patent 355,652.

Water is made more conductive, according to McCarty (U. S. Patent 736,868, Aug. 18, 1903), by the addition of tartrate of potassium, tartrate of sodium, or any of the citrates or other equivalents, and sulfuric acid. The apparatus (U. S. Patent 721,068, Feb. 17, 1903) consists of two tanks, connected by a pipe at about half their height. Each tank consists of an electrode, so located that the upper ends are about in a line with the axis of the connecting pipe, through which the current passes from one tank to the other. Each of the two tanks has an outlet at the top through which the gases generated may be led to suitable holders.

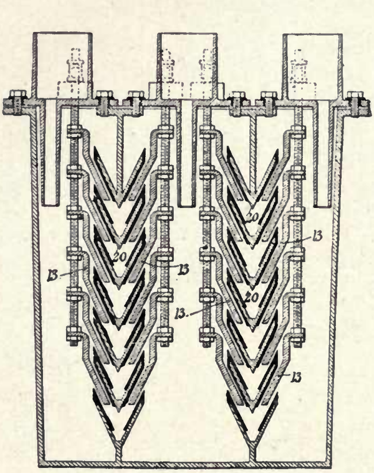


Fig. 130.

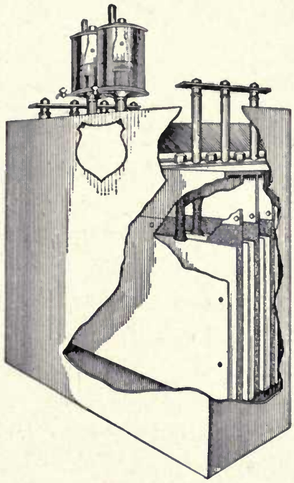


Fig. 131.

Another apparatus (McCarty, U. S. Patent 816,355, March 27, 1906) consists of two receptacles, each containing one electrode and connected by a conduit near the bottom. Each electrode is a plate of platinum coiled upon itself a number of times and has a projecting terminal portion directly opposite the end of the conduit. In still another type (McCarty, 814,155, March 6; see also 813,105, Feb. 20, 1906) the electrolytic cell is divided into two compartments by means of a solid diaphragm, which is perforated, short glass tubes being inserted in each perforation.

The **Burdett** system * of electrolytic apparatus consists of a varying number of generators or units, connected electrically in series. The unit, Fig. 131, comprises a container enclosing the electrodes and electrolyte, but the walls of the container do not function as electrodes. It is usually mounted on concrete foundations and is insulated both from the ground and from the generator proper. The electrodes are arranged on the multiple system, there being a number of both positive and negative electrodes in each unit. The electrodes are separated from each other by a partition of specially-prepared asbestos cloth which under the conditions of operation is permeable to the solution but not to gas.

* U. S. Patent to Burdett, 1,086,804, Feb. 10, 1914.

A bell or box casting, open at the bottom, is used for housing the electrodes and the asbestos diaphragm is stretched across the box casting from one side to the other, forming a number of compartments. In each of the compartments an electrode is placed running parallel to the asbestos curtain or diaphragm. The electrical connections are so arranged that commencing with and including the first electrode, every other electrode is a cathode, the alternate electrodes being anodes. At the top of the container the electrode terminals are joined by means of copper bus bars, thus bringing all the anodes to a common anode terminal and all of the cathodes to a similar connection.

The gas generated at the electrodes rises and is collected in the separate gas-tight compartments. These compartments are joined by two cored gas passages in the bell casting and the gases pass through these passages into and through glass indicators and purgers to the gas mains. Inserted in each of the service mains is a gas meter, a flash-back, and a water purger which removes the water held in suspension in the gas and at the same time acts as a pressure regulator for the generators. Purifiers are usually inserted in each line to cleanse the gas. The hydrogen and oxygen are led to their respective gasometers and from there are compressed into storage tanks for use. By means of controls the compression may be taken care of automatically.*

The automatic control feature of the Burdett apparatus is useful. By means of electrical regulating devices the entire electrolytic equipment is under automatic control. It also serves as a safety device, preventing over-generation of gas or undue pressure on any parts of the apparatus. The compressor, when the collecting gasometer reaches a predetermined height, will automatically start, and will stop when the gasometer falls to a predetermined level. Electric control is provided which will stop the motor of the compressor when the storage tank pressure reaches a certain point, starting the motor when the pressure falls again, and another control is provided which will stop the generation of gas when both gasometer and storage tank are charged to their full capacity.

Fig. 132 shows a battery of Burdett generators and Fig. 133 illustrates a complete equipment embracing motor-generator, gasometers, storage tanks and automatic control devices.

Each generator operating under a current of 400 amperes will produce in excess of 6 cubic feet of hydrogen and one-half this amount of oxygen per hour, or in round numbers, 150 cubic feet of hydrogen and 75 cubic feet of oxygen per 24-hour day

* The author is indebted to Mr. Paul Pleiss for a description of the Burdett generator, also for some data on the Garuti and Schuckert cells.

with the gas measured at 20° C. and 760 mm. It is desirable to operate the plant as continuously as possible and a run of 23 or 24 hours per day is recommended.

Each cell operating under normal conditions will require, with a solution temperature of 80° F. about 2 volts for the passage of 400 amperes. Thus each cell requires about 800 watts (0.8 kilowatt-hour) per hour to produce about 6 cubic feet of

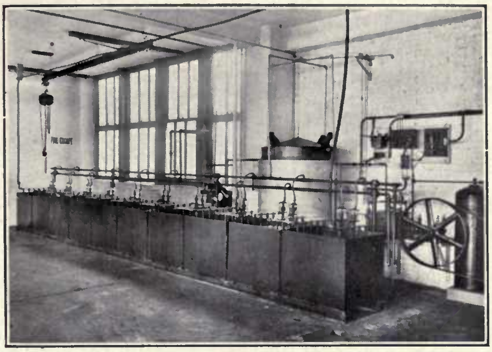


FIG. 132.

hydrogen per hour. The efficiency of the generator is therefore high. If the cell generator be artificially heated the consumption of electricity may be decreased by about 10 per cent with a corresponding increase in the efficiency of the unit. The hydrogen will average in purity 99 per cent or higher.

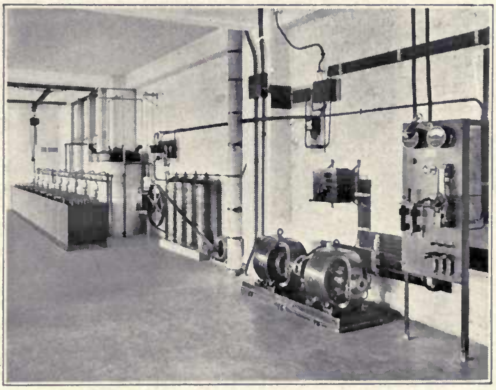


FIG. 133.

Electrolytic apparatus designed by **Hazard-Flamand** * is shown in Fig. 134. Between the inner and outer electrodes a porous diaphragm is inserted and a fluid seal is disposed about both sides of the top of the

* U. S. Patent 1,003,456, Sept. 19, 1911, assigned to the International Oxygen Co.

diaphragm and is composed of an outer seal and an inner seal, consisting of two concentric troughs one within the other. The electrolyte is fed into the inner trough, passes to the outer trough and is delivered from the latter on both sides of the diaphragm.*

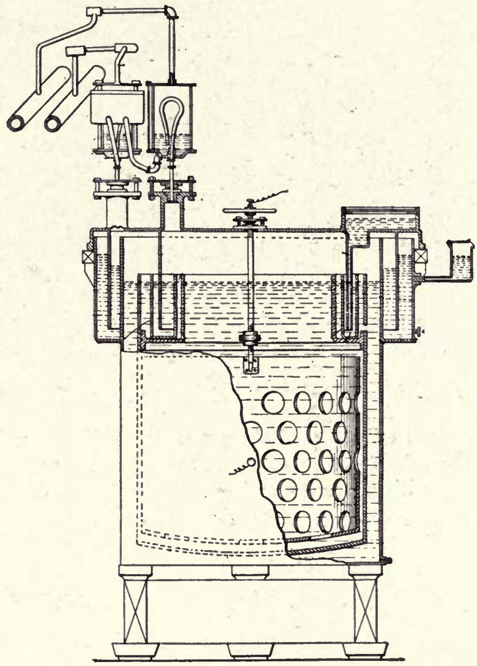


Fig. 134.

The **I. O. C. System (International Oxygen Co.)** is a well-standardized method of generating hydrogen and oxygen. The electrolytic cell used is very simple, an outside view being given in Fig. 135 and a diagram in Fig. 136. The iron tank or container serves as the cathode, being connected to the negative pole of the electric supply circuit. From the cover of this tank is suspended a perforated tank which serves as the anode, being connected to the positive pole of the supply circuit. It is made of a specially selected low-carbon steel, to prevent the formation of spongy rust. By means of an asbestos sack, suspended from the cover between anode and cathode, two separate compartments are formed. At the top these compartments are sealed by a hydraulic joint. Through an opening in the cover a solution of caustic alkali in distilled water is poured into the hydraulic

* See also U. S. Patent 646,281, March 27, 1900, to Hazard-Flamand.

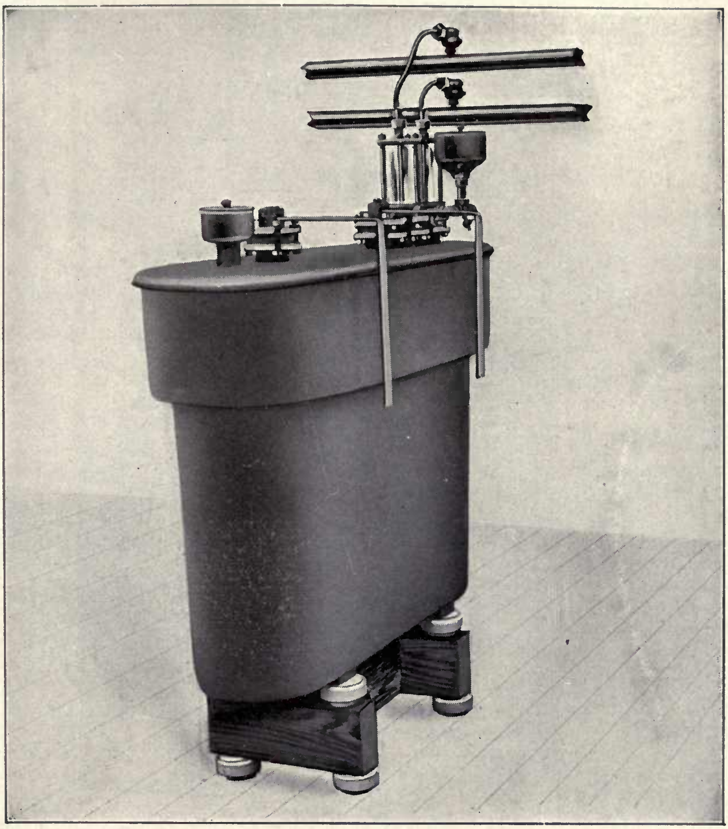


Fig. 135.

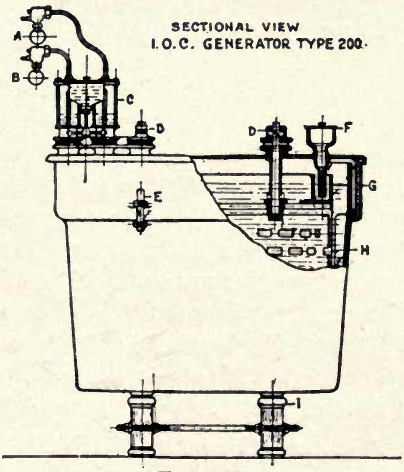


Fig. 136.

joint and distributed in the two compartments. The whole cell is placed on insulating supports of porcelain.

The oxygen and hydrogen gases evolved do not pass directly from their compartments to the off-take pipes, but first bubble through water contained in the two "lanterns" on top of the cell. They enable the operator to see at a glance how the cell is working. The purity of the gases produced is very high. A sample of hydrogen produced

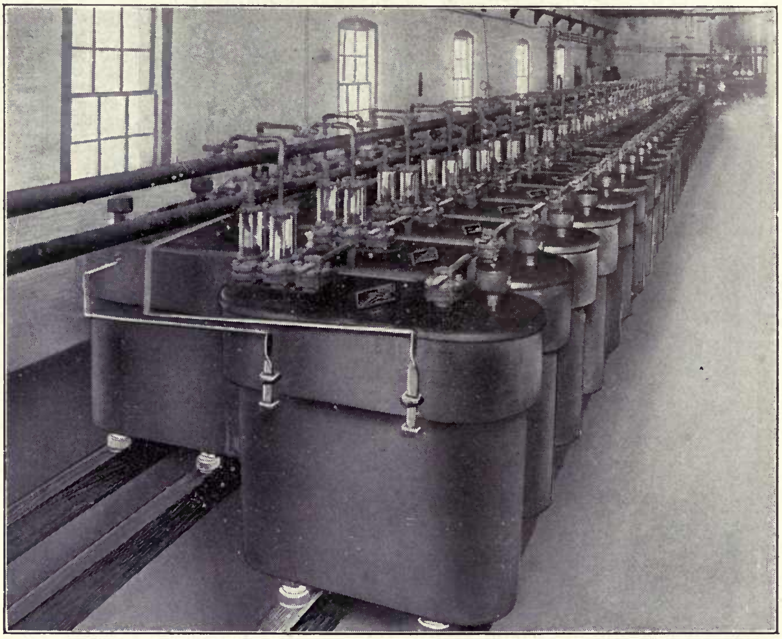


Fig. 137. Battery of I. O. C. generators.

by this electrolyzer, analyzed by the Conservatoire National des Art et Metier in Paris, showed 99.70 per cent hydrogen, the fraction of the impurities being so small that they were not examined.

All that is required for the operation of the cell is the daily addition of somewhat over a gallon of distilled water to make up for the quantity decomposed into hydrogen and oxygen. The daily output is approximately 72 cubic feet of oxygen and 144 cubic feet of hydrogen. As to the electrical energy requirements a joint test * made in November, 1910, by the Laboratoire Centrale de l'Electricite and the Conservatoire National des Arts et Metier with two unit cells of this type of electrolytic cell showed that the production of 1 cubic foot of oxy-

* Met. and Chem. Eng. (1911), 471.

gen and 2 cubic feet of hydrogen requires 0.2797 kilowatt-hour. Reversely 1 kilowatt-hour produces 3.54 cubic feet of oxygen and 7 cubic feet of hydrogen. Each unit cell requires a little above 2 volts and from 300 to 400 amperes. A current of 350 amperes produces about 65 cubic feet of oxygen and 130 cubic feet of hydrogen per day.

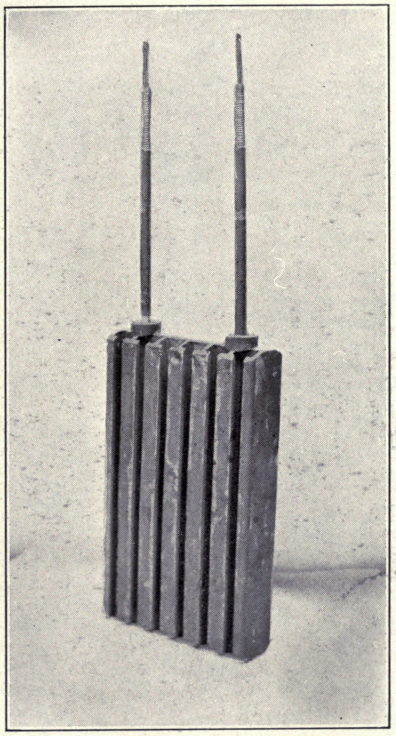


FIG. 138.

The following table gives the results of a test recently made by the Electrical Testing Laboratories of New York for the International Oxygen Co.

Cell No.	Average amperes	Average volts	Average watts	Maximum temp.	Purity of oxygen	Cubic feet per hour		Cubic feet per kilowatt-hour	
						Oxygen	Hydrogen	Oxygen	Hydrogen
8	405.1	2.388	967	31.8° C.	97.73%	3.247	6.184	3.358	6.395
14	405.0	2.562	1038	30.0° C.	98.67%	3.239	....	3.120	....
66	368.8	2.826	1042	32.0° C.	98.46%	2.886	5.788	2.770	5.555
70	392.0	2.660	1043	26.5° C.	98.50%	3.082	6.254	2.955	5.900
Average	392.7	2.609	1022	30.1° C.	98.34%	3.114	6.075	3.051	5.950

The four cells tested were selected as being representative of the entire battery after taking a set of preliminary electrical measurements on each of the cells.

All of the data given herewith are from readings as actually observed and corrected for instrument errors. Gas volumes are corrected for moisture and calculated to 20° C. and 760 mm.

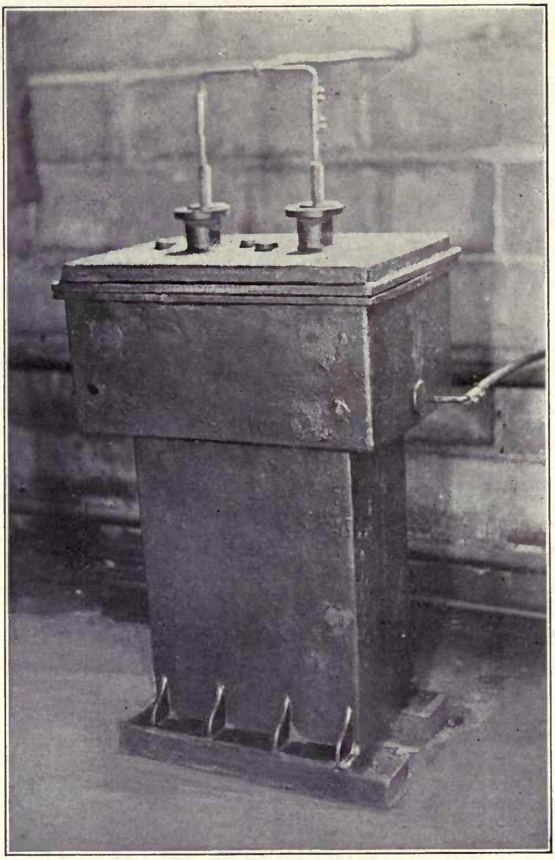


Fig. 139.

The main item of operating expense is the cost for the electric current. In New York City the wholesale rates are higher than in many other large cities and vary from 5 to 3 cents per kilowatt-hour, according to the size of the plant; since 1 kilowatt-hour produces about 3 cubic feet of oxygen and 6 cubic feet of hydrogen, the electric power cost for producing 1000 cubic feet of oxygen and at the same time 2000 cubic feet of hydrogen would be between $16.70 and $10.00. However, in large manufacturing plants which have their own power houses the cost of energy is much less; thus it is known that at the South Chicago works of the U. S. Steel Corporation the electrical energy supplied to the electric furnaces is charged at the rate of half

a cent per kilowatt-hour. At this rate the electric power cost for producing 1000 cubic feet of oxygen and 2000 cubic feet of hydrogen would be $1.67.

Besides the electric power cost there is the cost for distilled water and for attendance. The latter is a small item, and the cost for the distilled water which must be added to the cells to make up for the water electrolyzed may be calculated from the fact that a little over 6 gallons of distilled water are required to produce 1000 cubic feet of hydrogen.

One of the objections advanced against the electrolytic system is the relatively large floor space which it occupies, and to obtain an apparatus of a durable yet compact character the author has designed a generator having T-shaped ribs on both anode and cathode, affording a large generating surface without excessive bulk. Fig. 138 shows a form of anode and Fig. 139 the assembled generator.*

* U. S. Patent 1,087,937, Feb. 24, 1914.

CHAPTER XX

SAFETY DEVICES

The handling of electrolytically-derived gases brings with it the possibility of explosions due to accidental mixing of the two gases, and to guard against serious results, at frequent intervals in the connections of the apparatus and service pipes, safety devices should be inserted.

The common form of safety device is the wire-gauze arrangement of **Sir Humphrey Davy.** It usually consists of a roll of wire gauze or a number of disks of gauze inserted in the pipe connections. Such arrangements sometimes will check the progress of an explosion temporarily or completely, but as a rule when an explosion wave passes along the pipe in which the wire gauze is placed, although checked temporarily by the wire-gauze obstruction, it soon heats the latter to the ignition point. Thus the gas on the other side of the gauze is ignited and the explosion wave continues on its course.

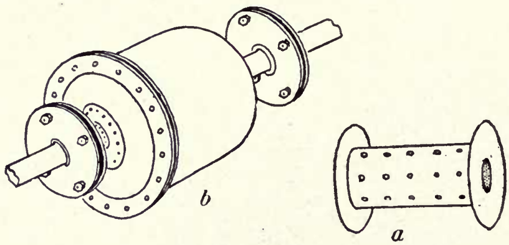


Fig. 140.

When wire gauze is used preferably it should take the form shown in Fig. 140. A spool *a* carries perforations along its stem and over this wire gauze is wound to make a thick layer. The spool is placed in the holder *b* and fitted tightly in place against a rubber gasket so that gases entering one end of *b* will pass along the hollow stem, flow through its perforations and those of the gauze and make their exit at the opposite end of *b*.

Glass wool obstructs explosion waves in a fairly satisfactory manner if it is inserted into the pipe connections in such a way as to fill the cross-sectional area without being packed so tightly as to greatly

reduce the flow of gas. Layers of glass wool, or finely-divided refractory material, such as fire-brick granules of about 20 mesh, alternated with bundles of wire gauze, may be packed into pipes of relatively large diameter to form an excellent safety device, which is rendered even more reliable if placed in a tank of water so as to be kept cool in event an explosion wave causes ignition of the gas at the surface of the outer layer.

It is stated by **Schoop** that under the conditions occurring in practice explosion mixtures are formed when either gas contains by volume 6 to 8 per cent of the other gas. Such an impurity may quite readily occur through injury to the diaphragm of cells of the asbestos-diaphragm type, and in constructions similar to the Garuti cell care should be taken to prevent an excess voltage which will render the diaphragms bipolar.

Boynton's device for preventing the transmission of explosions is shown in Fig. 141. *A* is the gas inlet, *B* the outlet, *E* one or more perforated plates and *H* a space filled with fragments of metal.*

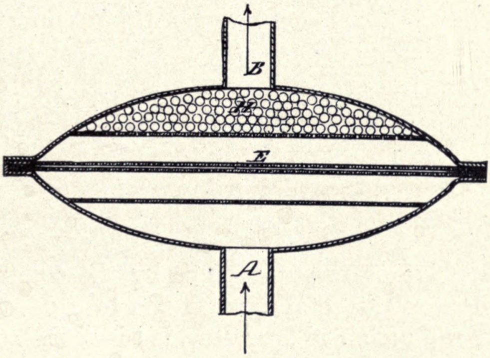


FIG. 141.

For the prevention of hydrogen explosions steel wool is recommended by **Ohmann.**† He regards steel wool as very suitable to take up and carry off the heat developed and, by lowering the temperature in this way, preventing the spreading of an explosion. To insure against the danger of an explosion, a roll of the wool, somewhat tightly pressed together, is placed in the gas conduit. Trials with a mixture of $\frac{2}{7}$ hydrogen and $\frac{5}{7}$ air, also with the strongest explosive gas mixture 2 H + O, showed that the explosive flame or wave was checked and extinguished in contact with the wool.

* U. S. Patent 58,055, Sept. 18, 1866. See also U. S. Patents 713,421, 730,807, 743,064, 819,202 and 948,323.

† Z. physik. chem. Unterricht, 11, 272; Chem. Zentr. (1912), 1, 1426.

The various possible causes of certain fatal accidents resulting from the explosion of oxygen or hydrogen cylinders has been discussed by **Bramkamp.***

In most cases it is certain that an explosive mixture of hydrogen and oxygen has been introduced into the cylinder. The two most important causes of this are: (1) the use of the same compressor alternately for both gases; and (2) unsatisfactory control and attention when the gases are obtained at the same time in the electrolysis of water. Other causes which may contribute but which are unlikely in themselves to account for an explosive mixture in a full cylinder are: (1) the use of an oxygen cylinder as a hydrogen cylinder or vice versa, without previously removing all the original gas; and (2) the absorption of hydrogen by finely-divided iron inside the cylinder. The various methods by which the explosive mixture when present may be exploded include: (1) ignition of oil or other combustible material in the valve or pressure gauge by the compressed oxygen; (2) local rise in temperature of the gas due to sudden closing of the valve; (3) catalytic action of finely-divided iron in causing combination in the mixture and raising its temperature; and (4) pyrophoric oxidation of finely-divided iron. Bramkamp is of the opinion that with suitable precautions an explosive mixture need never be put into a cylinder, and that all cylinders should be tested by analysis of their contents immediately after filling.

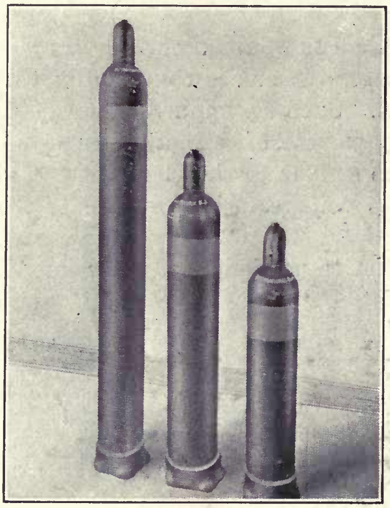


FIG. 142. High-pressure cylinders for hydrogen.

Tubes of compressed hydrogen, accidentally contaminated with air, have been known to explode on connecting them with a manometer for the purpose of measuring the pressure of the gas. **Lelarge** † has found that if ordinary manometers are employed in the usual way, such explosions may occur whenever the hydrogen contains enough air to render it explosive, and the pressure is sufficiently high. The reason probably lies in the rise of temperature produced by the sudden

* Zeit. ang. Chem. (1912), 536.

† Compt. rend. (1912), 914.

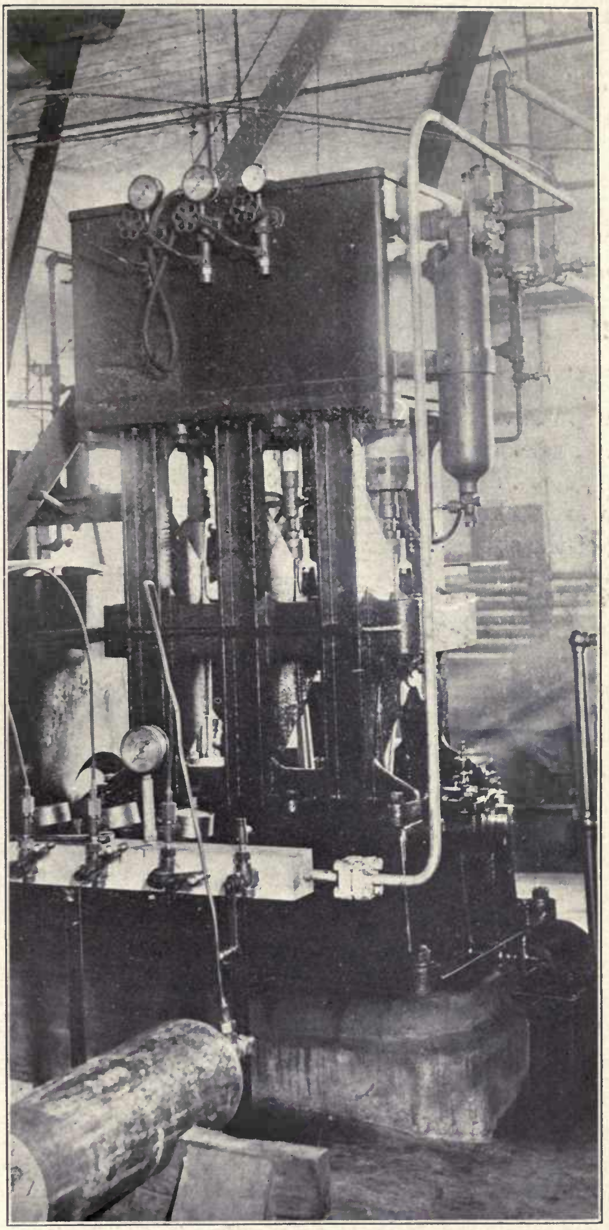


FIG. 143. Compressor for compressing hydrogen or oxygen into cylinders.

and more or less adiabatic compression of the air in the manometer. Such accidents may be avoided by interposing, between the tube of compressed gas and the manometer, a safety-tube containing discs of metallic gauze of such mass that they are not appreciably heated by combustion of the gas mixture in the manometer. By this means the ignition of the main body of gas is prevented. Similar safety-tubes should be employed whenever a highly-compressed explosive gas mixture is allowed to expand suddenly into a confined space. Before measuring the pressure of compressed hydrogen, liable to contain air or oxygen, it is advisable to determine its density, as a further safeguard.

Summary

The majority of the numerous proposals for making hydrogen in various ways have been outlined in the foregoing for the reason that many investigators at the present time are studying the subject of hydrogen generation, and everywhere present and prospective users of hydrogen are seeking information which may enable a better understanding of the subject.

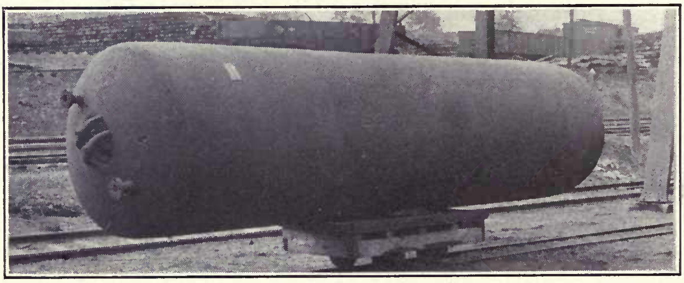


Fig. 144. Pressure tank for storage of hydrogen.

For oil hydrogenation at least four methods of generating hydrogen are likely to find a place. These are the (1) steam-iron, (2) water-gas liquefaction, (3) water-gas and lime and (4) electrolytic systems. With the exception of the latter these all require a water-gas plant with a not wholly simple system of purifiers, etc. As to the steam-iron method it may be noted that the opponents of this system claim it has been shown in practice that the iron sponge will not regenerate after a few operations and the iron retorts used are demolished all too soon by the high heat employed and have to be continually replaced. The advocates of the system claim great improvement in the matter of longevity of the iron sponge and also figure on a cost of production

around 90 cents to $1.00 per 1000 cubic feet of hydrogen. It is doubtful if this figure generally could be reached and so far as the author can ascertain the cost in this country with plants of moderate size is approximately $1.50 per M. The liquefaction system, although scarcely feasible to install in a small way, should prove attractive for large scale operation as the cost of production is not over $1.00 to $1.20 per M for gas of very fair purity. The objection has been raised that the by-product of carbon monoxide under high pressure is dangerous to handle. The water-gas and lime system from the point of view of low cost of operation has much in its favor, but has as yet received no extensive technical application. The electrolytic process may be called the foolproof system, as with proper safeguards against mixing of the gases and suitable safety devices, the generating plant may be operated with unskilled labor. The objections raised against it are the floor space required and the high cost of the gas. If, however, the oxygen is saved and compressed it can usually be sold at a profit which, credited against the hydrogen account, greatly reduces the cost of the latter. For small plants electrolysis has much in its favor.*

Purification of Hydrogen

In the previous discussion of methods of producing hydrogen various procedures of purification have been mentioned. To summarize,

* The cost of hydrogen per cubic meter (1 cubic meter = 35.3 cubic feet) produced in various ways is given by Sander (Zeitsch. f. angew. Chem. (1912), 2407) as follows:

Stationary Plants

	Cents
Acetylene (Carbonium)	3¾
Steam (Internat. Wasserstoff)	2½–5
Water gas (Griesheim-Elektron)	1¾–2½
Water gas (Linde-Frank-Caro)	2¾–3¼
Oil gas (Rincker and Wolter)	2¾–3½

Portable Plants

	Cents
Iron and sulfuric acid	12½–20
Aluminium and caustic soda	about 62½
Silicon and caustic soda	17½–20
Ferro-silicon and caustic soda	17½–20
Calcium hydride	about $1.00
Hydrogenite (Jaubert)	about 37½
Maricheau-Beaupre system	about 37½
Activated aluminium (Griesheim-Elektron)	about 45

Sachs (Zeitsch. f. angew. Chem. (1913), No. 94, 784) believes the cheapening of the cost of manufacture of hydrogen due to the demand for this gas in air ship practice is in part responsible for the rapid development of oil hardening processes.

oxygen may be eliminated by passing the gas through heated tubes containing copper turnings; carbon dioxide by exposure to hydrated lime, carbon monoxide by contact with soda lime at 300° C. or over, in the presence of moisture, or with acid cuprous chloride; and nitrogen may be removed by exposure to heated calcium carbide. Moisture may be reduced to a negligible amount by means of quicklime, calcium chloride or other desiccating agent.

Catalyzers of different types vary considerably in their resistance to impurities or catalyzer poisons in the hydrogen, but the period of activity of the more reliable catalyzers is at best all too short, and it may be laid down as a general rule that hydrogen free from moisture, oxygen, sulfur, phosphorus, chlorine, arsenic and cyanogen compounds should be employed. Of course there are exceptions to this, as, for example, with nickel oxide catalyzers oxygen is thought not to be detrimental and in fact by some is regarded as advantageous.

The **Badische Anilin und Soda-Fabrik** * remove traces of carbon monoxide from hydrogen by passing the gases through caustic alkali solutions at high temperatures and pressures, e.g., hydrogen containing 1 per cent of carbon monoxide is treated with (*a*) an 80 per cent solution of caustic soda at 50 atmospheres pressure at 260° C., or (*b*) a 25 per cent solution of caustic soda at 200 atmospheres pressure at 240° C.†

Hydrogen prepared from commercial zinc and acid, is bubbled through petroleum spirit cooled by liquid air. A temperature of 110° C., according to **Renard,**‡ suffices to insure the removal in this way of all the arseniuretted hydrogen even from a rapid stream of the gas.

Wentzki removes arseniuretted hydrogen from impure hydrogen by passing the gas upwards through a cylinder packed with a mixture of two parts of dry chloride of lime and one part of moist sand or other inert material. If the column of purification material be sufficiently high, the whole of the arsenic is retained. A small quantity of chlorine is set free, but can be removed by passing the hydrogen through a second cylinder packed with nearly dry slaked lime.§

Rabenalt ‖ purifies hydrogen by passing it into a solution of iodine through which an electric current is simultaneously conducted.

* French Patent 439,262, Jan. 22, 1912.

† By heating a solution of caustic alkali under a pressure greater than five atmospheres, hydrogen is freed from sulfur and sulfur compounds. (Badische, British Patent 14,509, June 23, 1913.)

‡ Compt. rend. (1903), 136 (22), 1317.

§ Chem. Ind. (1906), 405.

‖ U. S. Patent 1,034,646, Aug. 6, 1912.

For purifying electrolytic gases **Knowles** * uses the apparatus as shown in Fig. 145. The gas to be purified is first passed through an ordinary washer then through an explosion trap and finally enters the purifier proper. In its entry into the purifier the in-going gas is preheated by passage around the conduit through which the out-going gas and vapor is passing. In the purifying chamber the gas passes through contact material and water vapor is formed and is condensed and removed. In the illustration the web k supports grids l of porcelain on which the contact material is spread. Knowles states that when the apparatus is working properly no external heat is required on account of the rise in temperature caused by the condensation.

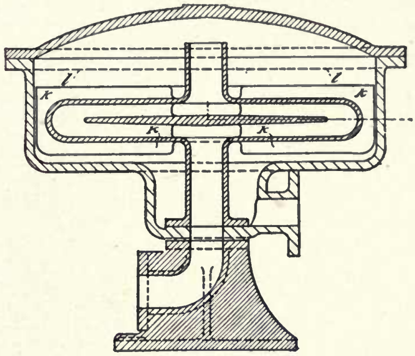


FIG. 145.

The removal of sulfur from gas by the **Carpenter** process † involves passing the gas over reduced nickel heated to 800° to 900° F. when carbon bisulfide reacts with hydrogen to form hydrogen sulfide and the latter body is absorbed in the usual manner.

The treatment of water gas to separate pure hydrogen, as described by **Frank**,‡ is of interest in this connection. Water gas, previously dried as much as possible, is conducted over calcium carbide, at a temperature from 300° C. up to the melting point of the carbide. When water gas is conducted over carbide thus heated an absorption of all the substances associated with the hydrogen takes place. Carbon monoxide or dioxide forms with the carbide, lime or carbonate of lime and carbon. The nitrogen is likewise absorbed. The hydrocarbons are decomposed when passed over the heated lime-carbon material with the separation of carbon. The action of the carbide on various gases is indicated by Frank in the following reactions:

$$CO + CaC_2 = CaO + 3\,C$$
$$CO_2 + 2\,CaC_2 = 2\,CaO + 5\,C$$
$$3\,CO_2 + 2\,CaC_2 = 2\,CaCO_3 + 5\,C$$
$$O + CaC_2 = CaO + 2\,C$$
$$2\,N + CaC_2 = CaN_2C + C$$

* U. S. Patent 1,073,246, Sept. 16, 1913.
† Jour. Ind. & Chem. Eng. (1914), 262.
‡ U. S. Patent 964,415, July 12, 1910.

$$SiH_4 + 3\,CO + CaC_2 + \text{heat} = CaSiO_3 + 5\,C + 4\,H$$
$$CS_2 + CaC_2 = 2\,CaS + 3\,C$$
$$H_2S + CaC_2 = CaS + C_2 + H_2$$
$$xPH_3 + CaC_2 = CaP_x + C_2 + 3\,xH$$
$$CS_2 + 2\,CO_2 + \text{heat} = 2\,SO_2 + 3\,C$$
$$2\,SO_2 + 3\,C + 2\,CaC_2 = CaSO_4 + CaS + 7\,C.$$

Almost chemically pure hydrogen is ultimately obtained as the final product. Carbon monoxide or dioxide may be previously entirely or partially removed from the water gas by mechanical separation of the constituent gases to relieve the carbide from the duty of separating the major part of the gases. If the water gas is produced at a high furnace temperature and contains in addition to hydrogen almost exclusively carbon monoxide and only a little carbon dioxide, the mechanical separation is preferably effected by conducting the water gas, which has been suitably cooled, into a Linde's air-liquefaction machine or other similarly constructed apparatus to liquefy the carbon monoxide; the dioxide and small quantities of silicon-hydrogen, etc., being obtained solid, whereas the hydrogen remains gaseous and can be separated and conducted away. If the water gas is produced at a low temperature, and if little carbon monoxide and principally carbon dioxide are obtained in addition to hydrogen, the previous mechanical separation may be effected by the water gas being cooled down to a temperature below that of the congealing or liquefying point of the secondary constituents of the water gas (carbon dioxide, carbon monoxide, etc.), these secondary constituents being separated in this manner in a solid or liquid form from the hydrogen which is obtained. After the previous mechanical separation of the secondary gases, the hydrogen which contains some remnant of other gases, as CO, CO_2, SiH_4, H_2S, PH_3, N, CS_2, and hydrocarbons, is then subjected to a final purification by conducting it over carbide. Before being passed over the carbide, the water gas may be freed from carbon dioxide and monoxide by treatment with lime and cuprous chloride solution respectively.*

* French Patent 371,814, Nov. 26, 1906.

APPENDIX

Hydrogenated Oil Patent Litigation

The general interest awakened by litigation in England over the Normann patent, together with the fact that the testimony given has brought out much of interest to investigators in the hydrogenation field, has led to the inclusion of a report of the Court proceedings which is here given substantially as published in the British Official Journal.

In the High Court of Justice. — Chancery Division

Before Mr. Justice Neville

Feb. 20 — Mar. 18, 1913

* Joseph Crosfield & Sons Ld. *v.* Techno-Chemical Laboratories Ld.

Patent. — Action for infringement. — Admissibility of expert evidence. — Construction of Specification. — Insufficiency of Specification — Patent held invalid. — Action dismissed. — Costs on the higher scale allowed.

In 1903 *a Patent was granted for a "Process for converting unsaturated "fatty acids or their glycerides into saturated compounds." The process consisted in treating the fatty bodies with hydrogen in the presence of a finely-divided metal, such as platinum, iron, cobalt, copper, and especially nickel, adapted to act as a catalyzer. The Specification stated that the saturation might be effected by causing vapours of fatty acid together with hydrogen to pass over the catalytic metal, but that it was sufficient to expose the fat or fatty acid in a liquid condition to the action of hydrogen and the catalyst. The Specification gave no details of the process, but after having given, in general terms, an example of the process, stated that the quantity of the nickel added and the temperature were immaterial, and would only affect the duration of the process. In an action for infringement of the Patent, the Plaintiffs contended that the publication of the fact that the process could be carried out with bodies in the liquid state*

* Supplement, June 18, 1913. The Illustrated Official Journal (Patents), Vol. XXX. Reports of Patent, Design and Trade Mark Cases. No. 12.

was of great merit; they claimed that the Patent was for a principle, and that, the Patentee having shown one way of putting it into practice, he was entitled to claim for all ways. The Defendants contended that the experiments of their witnesses showed that, for the success of the process, the catalyst must be prepared in a particular way and the process carried out with precautions not indicated in the Specification and requiring research for their ascertainment.

Held, *that the Patentee claimed the hydrogenation of all unsaturated fatty acids, and their glycerides, by the use of finely-divided platinum, iron, copper, and cobalt, as well as nickel, and that if the process failed as to any of the bodies to be hydrogenated or any of the catalysts the Patent was invalid; that no method of carrying the alleged invention into effect was sufficiently described in the Specification; and that the Patent was invalid. The action was dismissed with costs.*

On the 21st of January 1903 Letters Patent (No. 1515 of 1903) were granted to *Wilhelm Normann* for a " Process for converting unsatu-" rated fatty acids or their glycerides into saturated compounds."

The Complete Specification was as follows: — " The property of " finely-divided platinum, to exercise a catalytic action with hydro-" gen, as it does with oxygen, is already known. For instance, *Wilde* " observed the following reaction taking place in the presence of " platinum black: —

$$\text{“ } C_2H_2 + H_4 = CH_3 - CH_3$$
$$\text{“ } C_2H_4 + H_2 = CH_3 - CH_3$$

" and *Debus* noticed the reaction:

$$\text{“ } HCN + H_4 = CH_3NH_2$$

" Recently *Sabatier* and *Senderens* have discovered that other " finely-divided metals will also exercise a catalytic effect on hydro-" gen, *viz.* iron, cobalt, copper and especially nickel. By causing " acetylene, ethylene, or benzene vapour in mixture with hydrogen gas " to pass over one of the said metals, the said investigators obtained " from the unsaturated hydrocarbons saturated hydrocarbons, partly " with simultaneous condensation.

" I have found, that it is easy to convert by this catalytic method " unsaturated fatty acids into saturated acids. This may be effected " by causing vapours of fatty acid together with hydrogen to pass " over the catalytic metal, which is preferably distributed over a suit-" able support, such as pumice stone. It is sufficient, however, to " expose the fat or the fatty acid in a liquid condition to the action " of hydrogen and the catalytic substance. For instance, if fine nickel " powder obtained by reduction in a current of hydrogen, is added to

"chemically pure oleic acid, then the latter heated over an oil bath, "and a strong current of hydrogen is caused to pass through it for "a sufficient length of time, the oleic acid may be completely con- "verted into stearic acid. The quantity of the nickel thus added "and the temperature are immaterial and will only affect the dura- "tion of the process. Apart from the formation of small quantities "of nickel soap, which may be easily decomposed by dilute mineral "acids, the reaction passes off without any secondary reaction taking "place. The same nickel may be used repeatedly. Instead of pure "oleic acid, commercial fatty acids may be treated in the same "manner. The yellowish fatty acids of tallow, which melt between "44 and 48° C. and whose iodine number is 35.1, will, after hydro- "genation, melt between 56.5 and 59° C., while their iodine number "will be 9.8 and their colour slightly lighter than before, and they "will be very hard.

"The same method is applicable not only to free fatty acids, but "also to their glycerides occurring in nature, that is to say, the fats "and the oils. Olive oil will yield a hard tallow-like mass; linseed oil "and fish oil will give similar results.

"By the new method, all kinds of unsaturated fatty acids and their "glycerides may be easily hydrogenised. It is not necessary to "employ pure hydrogen for the purpose of the present invention; "commercial gas mixtures containing hydrogen, such as water gas, "may also be used."

The Patentee claimed:—"1. The process for converting unsatu- "rated fatty acids, or their glycerides, into saturated compounds, "which consists in treating the said fatty bodies with hydrogen in the "presence of a finely-divided metal adapted to act as a catalyser, "substantially as described. 2. The herein described manufacture "of saturated fatty compounds from unsaturated fatty acids, or their "glycerides, by means of water gas or similar gas mixtures."

On the 19th of December, 1911, *Joseph Crosfield & Sons Ld.* commenced an action for infringement of the Patent against *Techno-Chemical Laboratories Ld.* and *Nils Testrup*, claiming the usual relief.

The Plaintiffs by their Statement of Claim alleged that, (1) they were the owners of the Patent; (2) the Patent was valid and subsisting; (3) the Defendants had infringed and threatened and intended to infringe.

By their Particulars of Breaches they alleged that, (1) the Defendants had infringed by importing into, and by the manufacture, sale, offering for sale, supply and use in, this country of compounds made in accordance with the process described in the Specification and

claimed in both the Claims, and by the use in this country of the process; and (2), in particular, the Defendants, and each of them, had, on the 1st of December, 1911, caused to be treated with hydrogen in the presence of a finely-divided metal adapted to act as a catalyser, in their factory situate at "Fairlawn," Clapham Park, in the county of London, 9 kilogrammes of cotton oil, in infringement of both the Claims.

By their Defence the Defendants, (1) did not admit the allegations in paragraph 1 of the Statement of Claim; (2) denied that they, or either of them, had infringed or threatened or intended to infringe; and (3) said that the Patent was, and always had been, null and void.

By their amended Particulars of Objections they said that, (1) *Wilhelm Normann* was not the true and first inventor. (2) The alleged invention was not subject-matter for a valid Patent, by reason of the common and/or public knowledge at the date of the Patent. The Defendants would refer to all the prior publications set out in paragraph 4 below as disclosing part of the public knowledge. (3) The alleged invention was not useful. (4) The alleged invention had been published in this realm prior to the date of the Patent: — (i) By the deposit in the Patent Office Library of the following Specifications: (*a*) British: — *Lake* (No. 2798 of 1883) and *Ramage* (No. 7242 of 1901). (*b*) German: — *Zürrer* (No. 62,407). The whole of each of the Specifications was relied upon. (ii) By the sale and publication in the United Kingdom, and by the deposit in the Patent Office Library, of (*c*) "Comptes Rendus de l'Académie des Sciences," of Paris, vol. 133, dated 1901, pages 321–4, comprising an article entitled "Chimie "Organique. — Nouvelle méthode de préparation de l'aniline et des "alcalis analogues." Note de MM. *Paul Sabatier* et *J. B. Senderens.* (*d*) "Bulletin de la Société de Chimie," series 3, vol. 1, pages 295–6, comprising a communication entitled "No. 29. — Transformation de "l'acide oléique en acide stéarique" by *De Wilde* and *Reychler.* (*e*) "Journal of the Chemical Society," London, for the year 1889, vol. 56, part 2, page 1140, comprising an abstract of the communication of *De Wilde* and *Reychler.* (*f*) "*Watts's* Dictionary of Chemistry," edition 1892, vol. 3, page 637, column 2, lines 42–4. (*g*) "Sitzungs-"berichte der Kaiserlichen Akademie der Wissenschaften," Vienna, 1876, vol. 72, part II, pages 366–75, comprising a paper by *Guido Goldschmiedt,* entitled "Uber die Umwandlung von Säuren der Reihe "$C_nH_{2n-2}O_2$ in solche der Reihe $C_nH_{2n}O_2$. (5) The Complete Specification of the Patent did not particularly describe and ascertain the nature of the invention and in what manner the same was to be performed, and was insufficient and/or misleading in the following par-

ticulars: — (*a*) No useful result could be obtained by following the directions given in the Specification. (*b*) No process was described by which, as alleged, saturation of unsaturated fatty acids, or their glycerides, could be easily or at all effected. (*c*) No process was described by which fatty acids, or their glycerides, could be hydrogenised by the action of catalytic iron, copper, cobalt, nickel or platinum. (*d*) No process was described whereby hydrogenation of fatty acids, or their glycerides, could be effected without the formation of secondary products. (*e*) No process was described whereby any useful results could be obtained by the use of any of the finely-divided metals mentioned. (*f*) No process was described whereby fatty acids, or their glycerides, could, as suggested, be hydrogenised by treatment in a vaporised condition. (*g*) The treatment as described of oleic acid in the liquid condition did not result in complete saturation, as alleged, or in any practical or substantially useful saturation. (*h*) No sufficient directions were given as to the quality of catalyst, or the temperatures or times required to produce the alleged results, or as to what variations of those factors might be required for different catalysts, and those factors were not immaterial as to the alleged results. (*i*) The same catalyst could not be used repeatedly as described at page 2, lines 40 to 41. Alternatively, no sufficient directions were given to enable the same catalyst to be used repeatedly. (*j*) No useful result could be obtained by the use of commercial gas mixtures as described on page 3, lines 5 and 6. (*k*) No sufficient directions were given as to the preparation of nickel or other metal to be used as catalyst. (*l*) The statement on page 3, lines 3 and 4, of the Specification, namely, that by the new method all kinds of unsaturated fatty acids and their glycerides might be easily hydrogenised, was incorrect. (*m*) No sufficient directions were given as to which impurities might be present with, or as to which impurities must be excluded from, the hydrogen in order that the process might be carried out.

By their further and better Particulars the Defendants alleged that as to paragraph 5 (*l*) of their Particulars of Objections, the following would not be easily or at all hydrogenised: — Olive, linseed, fish, whale, rape, and cottonseed oils, or any fatty oils; oleic, erucic, linolic, linoleic, and ricinoleic acids, or any unsaturated fatty acids, by treatment in a vaporised or liquid condition by the alleged new method. And they alleged as to paragraph 5 (*m*) that the following impurities must be excluded from the hydrogen in order that the latter could, by any process, hydrogenise fatty acids or their glycerides: — Sulphur, sulphuretted hydrogen, and all other volatile sulphur compounds, arsenic, arseniuretted hydrogen and all other volatile arsenic com-

pounds, phosphorus, phosphoretted hydrogen and all other volatile phosphorus compounds, chlorine, oxygen, the oxides of nitrogen, ammonia, and empyreumatic substances obtained in the production of water gas.

Upon an application by the Plaintiffs for further and better Particulars as to paragraph 5 (*l*), the Defendants alleged that no fatty oils and no unsaturated fatty acid could be easily or at all hydrogenised in a vaporised or liquid condition by the Plaintiffs' process, and stated that they did not intend to offer any evidence of specific instances other than those specified in the Particulars.

In their Answers to Interrogatories the Defendant Company stated that, on the occasion of the visit of the Patentee to the Defendant Company's premises at Fairlawn, Clapham Park, on the 1st of December, 1911, to inspect a process for the hardening of fats, there was used a cylindrical autoclave 1 metre high and $\frac{3}{4}$ metre in diameter (inside measurements), with a steam jacket, and fitted with a non-conducting lining of unknown material. Nine kilograms of cotton oil were pumped into the autoclave, and 288 grams of a composition, containing a catalytic agent calculated on the oil, was used and was mixed with the oil prior to the introduction of the mixture into the autoclave. The autoclave was then filled with hydrogen from a cylinder to a pressure of 15 atmospheres. During the operation, the pressure varied from time to time according to the absorption of hydrogen. A mechanically driven circulation pump was connected with the autoclave both by its suction and delivery conduits. By means of a pump and a jet for spraying, a mixture of oil and composition containing the catalytic agent was drawn from, and forced back into, the autoclave. The iodine absorption was not determined. The composition containing the catalytic agent was prepared from a salt of nickel. The Defendant Company said that the catalyst was the subject of provisional protection (No. 4702 of 1912), and they objected to giving further particulars, but subsequently they said that the composition was prepared as follows: — About $1\frac{1}{2}$ kilograms of nickel sulphate was dissolved in about 3 litres of water, and about the same weight of sodium carbonate, dissolved in about the same quantity of water, and at about 70–80° C., was added to the nickel sulphate which was at about 60–70° C. The mixture was stirred for about $1\frac{1}{2}$–2 hours, and the precipitate was filtered off and washed with distilled water at about 25° C. for 60–70 hours alternately in tanks and filter press. A small sample was dried and tested to ascertain that the precipitate had been sufficiently washed. The washed precipitate was dried in hot air at 80–85° C., and was calculated to weigh 720

grams. It was then roasted in an iron frying pan for about 15 minutes over an open Bunsen gas burner, and the weight after roasting was calculated to be about 380 grams. The product was heated to about 300° C. for about 6 minutes in a current of hydrogen in revolving glass tubes slightly inclined, the precipitate being introduced at the higher end and through a spiral glass tube, and the hydrogen at the lower end. The product, which weighed 288 grams, was directly introduced into a small quantity of oil, which was mixed with the 9 kilos the following day.

The Defendants during the trial referred to the following papers: — *Moissan*, Oxides of nickel ("Annales de chimie et de physique," 1880, 5th series, vol. 21, page 238) — the exhibit A.L. 9; *Moissan and Moureu*, Action of acetylene on iron, &c. ("Comptes Rendus," 1896, vol. 122, 1st half year, page 1240) — the exhibit A.L. 9; *Sabatier and Senderens* in the "Comptes Rendus" (the exhibit A.L. 5), Action of nickel on ethylene (124 (1897), page 616); Action of nickel on ethylene: synthesis of ethane (*ib.*, page 1358); Hydrogenation of acetylene in the presence of nickel (128 (1899), page 1173); Action of copper on acetylene; formation of a very condensed hydrocarbon, cuprene (130 (1900), page 250); Hydrogenation of acetylene in the presence of copper (*ib.*, page 1559); Hydrogenation of acetylene in the presence of reduced iron or cobalt (*ib.*, page 1628); Hydrogenation of ethylene in the presence of various reduced metals (*ib.*, page 1761); Hydrogenation of acetylene and ethylene in the presence of divided platinum (131 (1900), page 40); Action of various divided metals, platinum, cobalt and iron, on acetylene and ethylene (*ib.* (1900), page 267); Direct hydrogenation effected in the presence of reduced nickel; preparation of hexahydrobenzene (132 (1901), page 210); General method of synthesis of the naphthenes (*ib.* (1901), page 566); Hydrogenation of various aromatic hydrocarbons (*ib.*, page 1254); new method of preparing aniline and analogous alkalies (133 (1901), page 321); direct hydrogenation of carbon oxides in the presence of various divided metals (134 (1902), page 689); Hydrogenation of ethylenic hydrocarbons by the contact method (*ib.*, page 1127); Synthesis of various petroleums: contribution to the theory of the formation of natural petroleums (*ib.*, page 1185); Direct hydrogenation of acetylenic hydrocarbons by the contact method (135 (1902), page 87); Direct hydrogenation of oxides of nitrogen by the contact method (*ib.*, page 278); and a paper by the same authors in the "Annales de chimie," &c., 8th series, vol. 4 (1905), page 5 — an exhibit marked J.L. 1.

Sir *A. Cripps* K.C. for the Plaintiffs. — The Plaintiffs are substantially *Brunner, Mond & Co.*, and the real Defendants are *Lever Bros.*

Ld. An important feature of the invention is that it has enabled fish oils, and particularly whale oil, to be used for soap-making, hardening it and destroying its smell. Before the Patent, it was not known that the catalytic hydrogenation of fatty acids or oils could be effected without alteration of the quantity of oxygen contained in the acids or oils. The Patentee did not discover any new method of using catalysts, but he used them successfully with bodies with which they had never been used before; and he found that catalysts could be used with substances, that could not be readily vaporised, by simply treating them in the liquid state. That had been thought impossible. It is alleged that the directions given in the Specification are insufficient, but the Patent is for a principle of wide scope and there is no need for minute directions, because the process will work under all conditions. The invention has effected a revolution in the soap-making industry, and the Patent is a master Patent. The Specification describes a way of putting the principle into practice. *Lake's* Specification deals merely with the extraction of glycerine from fatty substances, and has no bearing on the invention here; nor has *Ramage's* Specification, which relates only to the drying of oils, without any hydrogenation. *Zürrer's* process is merely for saturating fatty acids with chlorine, and then replacing the chlorine by hydrogen by heating under pressure with water and metals; there is no catalytic action. *Sabatier* and *Senderens* state generally the catalytic action of certain finely-divided metals in adding hydrogen to incomplete organic molecules, and then go on to deal with the substitution of hydrogen for oxygen. The Patentee's object is to keep the oxygen in the acids and oils, and to add hydrogen, and *Sabatier* would lead people away from that. The papers by *De Wilde* and *Reychler* and *Goldschmiedt* do not deal with catalytic processes at all. The Defendants allege non-utility, meaning that if the Patentee's directions are followed the result that he describes would not be obtained. Several of the allegations in paragraph 5 of the Particulars of Objections are mere general allegations that the Patentee's process will not work. Catalytic action was well known, and it was not necessary to give directions as to the mode of preparation of the catalysts. The claim is for the application of known catalytic methods to substances to which they had not been applied before — for obtaining an old product by a new method. The Patentee mentions nickel as a catalyst, as being the best metal for the purpose. A competent chemist would have no difficulty in finding what were the best temperatures and proportions.

Evidence was given in support of the Plaintiffs' case.

Dr. *A. Liebmann* stated that fats could not be vaporized. There

was nothing in literature as to anyone, prior to the date of the Patent, having acted with hydrogen as a catalyzer on a liquid; *Sabatier* had said the presence of the liquid was fatal and destroyed the catalyst. The liquid oils, after having been hardened and made into fats by the patented process, could be used for various purposes. In the case of the fish oils the disagreeable smell was destroyed, and cheap vegetable oils could be used for the manufacture of margarine, and oils could be rendered useful for soap-making or candle-making. Before 1903 it was known that it was impossible to obtain a vapour of a glyceride, and that a fatty acid could be distilled in super-heated steam, or under reduced pressure. Steam would probably oxidise the catalyst unless hydrogen was present, and it would be excluded from vaporisation. The witness had used a current of hydrogen for the vaporisation of fatty acids. He gave details of experiments he had successfully made in the application of the patented process.

Dr. *F. W. Passmore* stated, *inter alia,* that the great part of the invention was that it had shown the erroneous character of the old theory that anything that would tend to cover up the surface of the catalyst would destroy it, and had shown that it was possible to catalyse in fat.

Sir *James Dewar* also gave evidence.

Walter K.C. summed up the Plaintiffs' case. — *Moissan* and *Moureu* in 1896 dealt with the action on a mixture, of acetylene and hydrogen, of iron, nickel and cobalt prepared by reduction with hydrogen at as low a temperature as possible. They found that, when incandescence took place, part of the acetylene was polymerised, and part was split up. Their theory was that the porous state of the metal led to the condensation of the acetylene, and the evolution of heat, and that all bodies having that catalytic or pyrophoric structure must give an identical result. They referred, as to the precautions to be taken in obtaining the nickel, to the paper by *Moissan* in the "Annales de Chimie," 1880. Dr. *Passmore* said that he found instructions to obtain the hydrated oxide of nickel in a finely-divided state by precipitation from the nitrate, sulphate, or carbonate, and that the finely-divided nickel, obtained from that oxide by reduction at as low a temperature as possible, would be pyrophoric and decompose acetylene. *Sabatier* and *Senderens* continued *Moissan's* work, and, in their Papers on the action of nickel on ethylene, said that the reaction takes place with the catalytic nickel, with nickel reduced at a red heat, or even with nickel filings. Then they dealt with the conversion of ethylene into ethane by means of hydrogen and a catalytic agent. After that, they dealt with the hydrogenation of

acetylene in presence of nickel, and with the action of copper and of iron and cobalt on acetylene, and with the hydrogenation of ethylene in presence of various reduced metals, with the hydrogenation of benzene, and with the preparation of aniline from nitro-benzene and analogous nitro-bodies. The results show that it is impossible to say that the method that will act in some cases will act in others, or to see why the fatty acids do not wet or act upon the surface so as to inhibit the action of the catalyst. Nowhere throughout those Papers is there any work with other than pyrophoric bodies, except in the case of acetylene and ethylene. *Normann* continued the work. He referred to the literature telling how to prepare the catalysts, although he need not have done so, as the literature was part of the common stock of knowledge of chemists. He stated that the fatty acids, not their glycerides, may be treated in the vaporised condition. There is no mystery as to the method of converting them into vapours. It is a common operation to bubble hydrogen through a liquid, and get the vapour of the liquid mixed with hydrogen. And *Sabatier* described that method, and also the use of a capillary tube. Then came *Normann's* great discovery, that the fatty acids, and their glycerides, could be treated in the liquid condition. The explanation seems to be that the liquid does not wet the metal, just as oil will stick to metal and not to rock, and so float up the metal. As to the use of an oil-bath, that appliance is used when the temperature desired is from about 100° to 250°. All the experiments conducted at temperatures between these limits succeeded. No chemist would endeavour to obtain finely-divided nickel by first grinding the oxide. In some of the Defendants' experiments the oxide from which the nickel was obtained was ground; it ought to have been precipitated — grinding will not give the fineness required.

Astbury K.C. for the Defendants. — The precipitated oxide dries into a hard cake, that has to be ground. There is no evidence that *Normann's* process is useful. The solidification of oils in this country is only now coming into commercial use. An ordinary chemist might work on *Normann's* process for years, and obtain no useful result at all. The Specification is deficient as to any valuable directions, and is misleading. To obtain a useful result something must be done that is not even hinted at in the Specification or in *Sabatier's* papers. A catalyst that will work with one sample of some particular fatty acid or glyceride will not work with another sample. The whole matter is mysterious. *Sabatier* did not use the pyrophoric metal used by *Moissan,* and the Specification ought to have given directions on the point. The Specification may be construed as

saying that fats may be treated in the vaporised state, though it is sufficient for them to be treated in the liquid condition; and it is admitted that fats cannot be vaporised. The nickel used by the Defendants has been obtained by the ordinary process of reduction in hydrogen, and, if that is not sufficient, the Patent is invalid for insufficiency of the Specification. The Patentee says the temperature is immaterial, but no one has used a temperature below 100°, and some of *Sabatier's* processes take place in the cold. If *Normann* had tried besides nickel, iron, cobalt, and copper, he would have found out certain differences between their action and that of nickel, and in that case he ought to have disclosed the best method of carrying out the process. He says that water-gas may be used; that means commercial water-gas, which contains sulphuretted hydrogen and cannot be successfully used. The Claim is for applying catalysis to the fatty bodies by vaporising or by the liquid process. The Plaintiffs' witnesses state that if one makes reduced nickel by the processes described in the text-books one will fail, and Dr. *Liebmann* went so far as to say that one would probably fail if one bought nickel oxide in a shop and reduced it as told by *Sabatier.* The Plaintiffs say their case stands or falls on being able to confine their Patent to preparing the catalyst by the particular method described in *Sabatier's* and *Moissan's* papers. But *Moissan* describes the reduction of the hydrated sesquioxide of nickel obtained by the action of chlorine on the hydrate of nickel protoxide and neither *Sabatier* nor *Normann* suggests that it is necessary to use the oxide prepared in that way. The use of chlorine would " poison " the catalyst. The Plaintiffs say that the nickel, to be catalytic, must be pyrophoric, but pyrophoric nickel will not act in some cases. For some unexplained reason, it will harden one sample, say, of linseed oil, but not another sample. The action depends on the mode of preparation of the body from which the oxide is made, on something in the fatty body, and on the temperature. *Sabatier* is actually misleading, as he did not say that it is material how the oxide is made, and he did not say anything about the mode of preparing the bodies from which the oxide is obtained. Mr. *Ballantyne* followed *Normann, Sabatier,* and *Moissan* and failed in every case. Then he had a suggestion from the Defendant *Testrup,* not given by the Plaintiffs' authorities, and in some cases he succeeded and in some he failed. He had found a similar result in repeating Dr. *Passmore's* experiments. Iron with acetylene is very pyrophoric, but iron as a catalyst for hydrogenation is practically useless; it will not act at all with liquids. The temperature at which the catalyst is prepared is immaterial except as to acetylene. *Sabatier* said that

the catalytic decomposition of ethylene takes place very well if the nickel has been reduced at a red heat, and in that case it is not pyrophoric. But the nickel is not so active as if it had been reduced at 300°, which is not *Moissan's* temperature. A chemist reading *Sabatier's* Papers would conclude that the density of the nickel is not increased by higher temperature, whether it is partly in the reduction or in the next process. *Sabatier* says the nickel must be freshly reduced; the Defendants have always freshly reduced theirs. He says that acetylene can be hydrogenised by sheet copper. There is not a single suggestion in *Sabatier's* Papers that one is to reduce from a hydrate, and from a body that itself has been prepared at a low temperature, and still less is there any suggestion that the temperature of reduction in any case should be *Moissan's* 240°, instead of 300°. The Specification is capable of being construed as meaning that the vapour process is applicable to the fats as well as to the fatty acids, that the expression "fatty acids," when used alone, stands both for the acids and their glycerides, the fats. The Patentee either knew, or did not know, that *Sabatier's* method would not act, that it was necessary to adopt *Moissan's* method of reduction from a higher oxide at a low temperature, and that the hydrate, instead of the oxide, must be used. If he knew any one of those three matters, which are essential to success, he has not mentioned them; if he did not know them, then he has not made an invention. And, even if the catalyst is prepared by the Plaintiffs' method, with certain of the fats and fatty bodies, no result is obtained. To infringe a master Patent by the use of an equivalent, the equivalent must be known at the date of the Patent to be an equivalent. In 1903 it was not known that, in acting catalytically on a liquid, it was equivalent to bubbling hydrogen through the liquid to take a fatty body and the metal and spray them into a chamber containing hydrogen under pressure, for it is admitted that no catalysis of a liquid was known at all, and none of the witnesses knew of any process, catalytic or other, in which the metal and body were sprayed together, or any liquid with metal in suspension in it was sprayed into a gas under pressure. That is an invention of *Testrup*, and will give results that the Patentee's process will not give. The Patentee says that temperatures are unimportant; *Sabatier* says they are most important; they vary greatly with each catalyst and body acted on; it is impossible to get any general law out of *Sabatier* at all. There is no evidence that the patented process has ever been worked.

Evidence was given in support of the Defendants' case.

H. Ballantyne, in answer to questions dealing with the point whether

a chemist would know that by obtaining nickel oxide through the hydroxide by precipitation, he would get the oxide in a more porous form, stated that a chemist could get the oxide in a bulky but finely-divided state, and that he would know that he would have a more finely-divided material than if he went to a higher temperature. The witness said that, as to specimens of nickel reduced from the oxide and nickel reduced from the carbonate, the latter would be more bulky, and more finely-divided, but would have a larger particle; the two specimens could both be sufficiently rapidly permeated by a gas, and the denser of the two would have better pyrophoric properties than the other, but pyrophoric activity was independent of catalytic activity; in the case of the hydrogenation of oil one is dealing with a liquid getting into a porous body. When the nickel oxide was reduced, nickel would, by the removal of the oxygen, be left in a cavernous condition, though there might be some contraction.

O. Hehner stated, that he had made a series of experiments — in which he used the purest oleic acid, and 2 per cent of the most active nickel reduced at 360° from purest nickel oxide for three hours. The rate of hydrogen flow was about 14 litres per hour, and the depth of the oil column 4 inches and the width $1\frac{3}{8}$ inches. The temperatures throughout the respective experiments were 90°, 100°, 120°, and 150°. The original iodine absorption was 86.4 per cent. After 18 hours 10 minutes, it was reduced in experiment (3) to 85.1 and in (4) to 81.7, in (5) to 82.9, and in (6) to 61.8; and in the last experiment, after 57 hours 5 minutes, it was reduced to 45.5.

Dr. *Julius Lewkowitsch* stated, that before 1903 he had read *Sabatier's* earlier Papers and had tried to hydrogenate oleic acid, as vapour and as liquid, with nickel; but had failed. He had prepared the nickel by converting the sulphate into carbonate, converting that into oxide, and reducing the oxide at 400° or a little above. Then he had read the Specification, but had again failed. Later he had read *Sabatier's* Paper of 1905 and had succeeded after two years' work.

O. Hehner, recalled, stated, that, in preparing the nickel he used, he had made the green hydroxide, and treated it with chlorine, obtaining *Moissan's* sesquioxide.

Dr. *A. Liebmann*, recalled, stated in cross-examination, that he had made a number of further experiments. For one, he had bought nickel protoxide, reduced it at 300°–320° C., and used it for the hydrogenation of oleic acid and had succeeded.

Jenkins K.C. summed up the Defendants case. — The Patent is invalid, first, because the Patentee claims a process for converting unsaturated fatty acids into saturated compounds by a catalytic

method applied to the vapours of the fatty acids, which process is not useful; secondly, because he claims a process for converting unsaturated fatty acids, or their glycerides, into saturated compounds by a catalytic method applied to the vapours of the glycerides, which process is impossible; thirdly, because he claims the substitution of commercial gas mixtures for hydrogen in carrying out his processes, whereas the use of those gas mixtures renders the processes, if otherwise practicable, impracticable unless the mixtures are purified, and he gives no directions for their purification; fourthly, because he claims a catalytic method wherein metals other than nickel, and particularly iron, cobalt, copper, and platinum, are employed as the catalysers, which processes are impossible or impracticable; or, alternatively, the Specification is insufficient and misleading in that no sufficient directions are given as to the catalytic substance necessary to be employed to enable the invention to be carried out; and, fifthly, because the Specification is insufficient in that no sufficient directions are given to enable the invention to be performed so far as the same relates to the processes claimed for the conversion of unsaturated fatty acids or their glycerides in a liquid condition into saturated compounds. The first four reasons depend to a great extent upon construction, and do not involve much dispute as to facts. If any one of them is valid, it is possible that the Patent might be made good by amendment, but if the fifth reason — the broad attack — is valid then the Patent could not be made good by any amendment. If the Defendants succeed on any one of these points they are entitled to have the action dismissed. The first objection assumes, for the purpose of argument, that the Specification tells how the process can be carried out, but asserts that when carried out it is useless. As to the vapour process, the Patentee seemed not to know that the fats cannot be vaporized, as, in 1912, he applied for a Patent in the Transvaal and said in his Declaration that the glycerides might be exposed in a vaporised condition to the action of the hydrogen and catalyst. With regard to the use of commercial gas, which is the subject of a separate Claim, *Sabatier* removed the sulphuretted hydrogen that would be fatal to the process, but the Patentee gives the impression that purification is not necessary. The Defendants have shown that one cannot, by using iron, cobalt, copper or platinum as catalysts, bring about the hydrogenation. The Plaintiffs' witnesses say that they have effected the hydrogenation with iron, cobalt and copper in the vapour process; but the Defendants have shown that one cannot succeed with these metals or platinum in the liquid process. If the Patentee claims hydrogenation in the liquid process by a metal other than nickel,

the Patent is invalid. With regard to platinum black, the Plaintiffs have not shown that it will work with anything. They say that it is not material, that is a question of construction; and the Defendants say that the Claim includes finely-divided platinum. As to the general scope of the Specification, the expression " this catalytic method " means the use of the finely-divided metals to exercise a catalytic action with hydrogen as they did with oxygen. The Plaintiffs seemed to think that *Sabatier's* Papers were to be treated as if the Patentee had recited them, but that is a false construction. He did not recite them, but he recited prior knowledge so far as was known to him, and exhaustively, as he mentions platinum black, and makes it clear that he may include platinum sponge. Then he gives general directions that it is sufficient to expose the fat or fatty acid, in a liquid condition, to the action of hydrogen and the catalytic substance. That is the Patentee's claim. It is not narrowed by what follows. The Patentee has thrown his net very widely, and has taken a correspondingly heavy burden. He thought he had discovered a new principle, and had found that the supposed capriciousness of catalytic action did not exist. The Plaintiffs have been working on this subject for years, but they have not told the Court what they have been doing. It is difficult to avoid reading their subsequently-acquired knowledge into the knowledge of 1903. It may be said that the Patentee has prescribed, in a loose way, a range of temperature from 100° to 250° — the range of an ordinary oil-bath; but he has stated that the reaction will be obtained at 100° with every body treated. And, as he says that temperature is immaterial, he has not purported to give any range of temperature. The Plaintiffs have to choose between saying that the statement that temperature is immaterial is of general application, in which case the Patent is clearly bad, and saying that the direction merely refers to the instance given, of nickel, and that the statement means that having found a temperature at which the reaction is obtained, it is immaterial whether or not one goes higher. The instance, and the direction as to the oil-bath are not of the essence of the invention. It has been proved that the temperature and the proportions are vital. As to the water-gas, if one purifies it, one does something that makes the hydrogen operative, and so the process comes within Claim 1. If the words " temperature is immaterial " are of general application to the Specification, they are misleading and invalidate the Patent; if they refer only to the specific instance then the Specification is insufficient as to the general process. The differences of opinion between the experts have been narrowed down to the mode of preparation of the catalyst — the nickel. Mr. *Hehner*

used temperatures of about 300° for the reduction of the oxide, and sometimes went to 340°; Dr. *Liebmann* went as high as 360° in one case. The question is further narrowed down to the preparation of the oxide. The process can be carried out with finely-divided metal obtained from any oxide, but only with certain bodies, and with certain precautions. *Moissan's* Papers have no bearing on the matter. His Paper of 1880 was simply directed to the investigation of the allotropy of certain oxides. The experiments of the Plaintiffs' witnesses had, in order to succeed, to be conducted with special stirring apparatus and a strong current of hydrogen, precautions that are not indicated by the Patentee. The failure of Dr. *Lewkowitsch* to obtain *Normann's* results, although following his Specification carefully, shows that the Specification is insufficient. The Patentee assumed that the catalyst that would act with the gases would act with the liquids, and it turned out that it would not. As to infringement, the Defendants' method is an improvement on the Patentee's, and if his claim is limited to his precise description, it is not an equivalent.

Sir *A. Cripps* K.C. replied. — As to the knowledge at the date of the Patent, the references to *Sabatier* imply a reference to *Moissan,* and *Sabatier* says that the best method is to prepare the catalyst in the way described by *Moissan,* that is, in order to get a porous oxide, hydrate should be used. The Plaintiffs' witnesses went through the sesquioxide and the hydrate to the protoxide, and showed that the process worked best in that way. They tried further experiments with oxides made from the carbonate, sulphate, and nitrate, and succeeded. The invention is of enormous value; it is said to be worth a quarter of a million a year; and there can be no question as to utility, or as to the sufficiency of the statement of the invention. The only question is as to the sufficiency of the directions. The stirrer and the strong current of hydrogen used by the Plaintiffs' witnesses were expedients such as would naturally be adopted by a chemist wishing to get contact between the reagents. Supposing the invention to be the hydrogenation of unsaturated fatty acids, and oils so as to saturate them, and the Patentee gives one example that works, that is sufficient. Possible complications with different catalysts have nothing to do with the matter. With regard to the presence of sulphuretted hydrogen in water-gas or illuminating gas, a chemist would know that sulphur is a " poison " to the catalyst and would remove it from the water-gas, and it is not found in modern illuminating gas. The direction that the catalyst is to be finely divided is sufficient to indicate that it is to be as finely divided as possible. The use in the

Claim of the expression "adapted to act as a catalyst" has been objected to, but such a description is properly employed in a claim for a wide principle. The further experiments of Dr. *Liebmann* and Dr. *Passmore* were conducted in accordance with the directions given in the Specification. They started with a fine nickel powder obtained by reduction in a current of hydrogen, added to it oleic acid, as pure as possible, heated it over an oil bath and passed a strong current of hydrogen through it, so as to keep the metal in a state of suspension. They succeeded, and the only objection made is that they added stirring, but that is an expedient that would naturally and properly be adopted.

Neville J. — The Specification in the present case is short and inartificial. The Patentee discloses, I think, clearly enough what he claims to have discovered. It was, in the first instance, that the saturation by hydrogen or hydrogenation of unsaturated fatty acids and their glycerides, fats and oils, could be attained by catalysis. In introducing his discovery, he refers to the fact that it had already been disclosed that, in certain cases, catalytic action with hydrogen had been brought about by the presence of finely-divided platinum, and further that *Sabatier* and *Senderens* had extended discovery in this direction by showing that other finely-divided metals, namely, iron, cobalt, copper, and especially nickel, might take the place of platinum. He tells us that *Sabatier* — I will use this name as including *Senderens* — obtained saturated hydrocarbons from unsaturated hydrocarbons (partly with simultaneous condensation, which I take to mean what he calls later secondary reactions), namely, acetylene, ethylene, or benzene, by causing their vapours mixed with hydrogen gas to pass over one of the said metals. Reading the Specification as a whole, I think he then proceeds to tell us that his discovery is that it is easy by "this catalytic method" — which means, I think, hydrogenation by catalysis — to hydrogenise all kinds of unsaturated fatty acids and their glycerides, that is to say, fats and oils. I may say, in passing, that the glyceride is merely the fatty acid with the addition of glycerine, and the fats and oils, thus composed, differ from the fatty acids in this respect, that while fatty acids may, under certain conditions be vaporised, fats and oils cannot. How to vaporise a fatty acid the Specification does not tell us, but *Normann* says that hydrogenation of the unsaturated fatty acid may be obtained by causing it in vapour with hydrogen to pass over the catalytic metal. This vaporisation, however, he declares to be unnecessary, since it is sufficient to expose the fat or fatty acid — that is to say, any unsaturated fatty acid or its glyceride — in a liquid condition to the action of hydrogen and the

catalytic substance. The evidence shows the advantage of treating the fats and fatty acids in the liquid state without vaporisation to be very great, and I think *Normann* did not intend to indicate vaporisation as part of his process, but to point out that you could obtain hydrogenation by a far simpler method. To dismiss this point at the outset, I do not think, upon any construction of the Specification, that the difficulty of vaporisation, even if it were as great as the Defendants suggest, would avoid the Patent. If the Specification is sufficient in other respects, what *Normann* here says is true, and, even if the process by vaporisation is of no commercial value, the liquid process is, and I think the Patent would stand. Having told us that treatment in the liquid state suffices, *Normann* discloses an instance in which he alleges that pure oleic acid may be completely converted into stearic acid, that is, a non-saturated fatty acid into a saturated fatty acid. I think, if he has described a process by which this may be done, and if that process is effective with all fats and oils and all other fatty acids in combination with any " finely-divided metal adapted to act as a catalyser " (including platinum, iron, cobalt, copper, and nickel), the Specification would be sufficient. Indeed, I should be inclined to hold that, if the invention was substantially co-extensive with the Claim, proof that some fatty acid or oil could not be successfully treated by one or more of the catalysers mentioned was immaterial, so long as the exception was of no commercial importance.

There are minor points upon the construction of the Specification raised, such as the possibility of using commercial gas mixtures as a substitute for hydrogen, but I will, in the first instance, examine the question of whether the process which *Normann* describes will effect the result which he claims for it, and I will here say that, if by his process a substantial saturation is effected, sufficient for technical purposes, I should not consider its failure to ensure complete saturation fatal, notwithstanding that he has stated that the oleic acid may be completely converted into stearic acid; nor should I think it fatal if some secondary reaction took place, notwithstanding his declaration to the contrary, so long as such reactions did not substantially interfere with the utility of the process.

In my judgment, the right of a Patentee to his monopoly is essentially a matter of substance, and the question to be decided a broad one, namely, whether he has in substance given the consideration which the grant of the Patent requires.

Now let us turn to *Normann's* Specification and see what are the conditions to be fulfilled to obtain the result which he indicates. First of all, nickel powder obtained by reduction in a current of hydrogen is

to be procured. There is no special meaning, I think, to be attached to the word "powder," except that the product is to be in a fine state of division; but the evidence shows that, if metallic nickel is to be obtained by reduction, it must be obtained by reduction of the oxide; so we take finely-divided nickel obtained by reduction of nickel oxide in hydrogen and add it to chemically pure oleic acid. For pure oleic acid, we may substitute any commercial fatty acid, or fat, so far as the method is concerned; though, of course, if we do, we cannot expect complete conversion of the whole compound, inasmuch as impurities may be expected. Then the oleic acid is to be heated over an oil-bath. No temperature is mentioned. The ordinary temperatures for which oil-baths are used are variously stated as extending from 50° or 100° to 250° C., but, inasmuch as the inventor tells us immediately after that the quantity of nickel added and the temperature are immaterial and will only affect the duration of the process, I think it is impossible to construe the Specification as giving any direction as to the temperature to be employed, unless, perhaps, one may say that, as heating is directed, it should be something above room temperature — how much, I think, one does not learn. A strong current of hydrogen is to be passed through the mixture, and I think it is common ground that the current should be strong enough to keep the metallic nickel suspended in the liquid in order to give the opportunity of contact between the surface of the nickel and the molecules of the other bodies.

Before proceeding further, I will put in untechnical language what I understand from the evidence to be conveyed by the word "catalysis." It appears that in the presence of, or in contact with, certain metals, chemical bodies undergo changes which do not otherwise take place. The reactions induced by the presence of the catalyst may involve merely the splitting up of a single chemical body, of which the decomposition of acetylene in the presence of finely-divided nickel is an instance, or the combination of two chemical bodies which, but for contact with the catalyst, would have retained their composition unchanged, although in contact with one another. The hydrogenation of a fatty acid where hydrogen and the fatty acid are brought into contact in the presence of a suitable catalyst is an instance of the latter kind of reactions, and that which forms the subject-matter of the present invention.

To return to the Specification, the experiments made by Mr. *Ballantyne* and Mr. *Hehner* show that you may take finely-divided nickel, or nickel powder, obtained by reduction from the oxide in a current of hydrogen, and add it to pure oleic acid or any other fatty acid, warm the mixture, and pass through it a strong current of hydro-

gen, without obtaining the catalytic reaction indicated by the Patentee at all. That, by preparing your nickel powder in a special way and raising the temperature to a certain degree, you may obtain the result required, although the reaction appears to be very capricious, is shown by the experiments of Dr. *Liebmann* and Dr. *Passmore* and admitted by Mr. *Ballantyne.* The Plaintiffs' contention is that the success of Dr. *Liebmann* and Dr. *Passmore* is conclusive to establish the validity of the Patent, for it is said that these gentlemen did no more than the Specification directed. They say that it was known in 1903 that catalysis was a surface or contact action, and that, for the purpose of obtaining contact, the finer the division the better the chance, and that it was known that, for the purpose of catalysis, the oxide should be reduced to the metal at the lowest possible temperature, or at about 300° C. Therefore, they say that any competent chemist upon reading the Specification would, as of course, take nickel oxide as finely-divided as possible, and reduce it in hydrogen at a temperature of from 300° to 350°.

I pause here to state certain conclusions at which I have arrived upon the evidence. It appears that the fineness of division of the nickel — by which is meant the minuteness of the pieces composing the substance, depends — not upon the temperature (within the ranges of temperature which are dealt with here) at which the oxide is reduced to the metal, but upon the physical state of the oxide with regard to minuteness of division at the time when the reduction commences, the number of pieces of metal after the reduction being substantially the same as the number of pieces in the oxide. Therefore, the temperature at which the reduction takes place is in this connection immaterial. The activity of a catalyst does not, however, I think, depend solely upon minuteness of division, but upon the porosity of the pieces of metal composing the powder. In the course of reduction, when the oxide gives up its oxygen, the metal left behind is in a porous, or what has been described as a cavernous condition, the result being that, inasmuch as the fatty substance may be able to penetrate into the cavities, a greater surface is afforded for contact than if it were in a denser or more solid condition. This distinction has, I think, not been sufficiently regarded in some parts of the evidence, the words "finely-divided" having been sometimes used to denote porosity, rather than the smallness of the pieces into which the metal is divided. Mr. *Ballantyne,* explaining the different qualities required for pyrophoric purposes and catalytic purposes, speaks of metal in larger particles or grains being more finely-divided than metal in smaller particles or grains. I do not think that, in fact, the words

"finely-divided" have a meaning in chemistry different from that which they bear in English. The effect of heating is to cause the porous metal to contract and become denser; hence the desirability of reducing the oxide at a low temperature; and I think to-day it would be common ground that the most promising catalyst for hydrogenation would be a suitable metal in the highest state both of fine division and porosity. At the same time, it must be remembered that this so-called catalysis remains unexplained. All that is known about it is, that it happens, and no one can safely predict what will happen in any case not already tested by experiment. Nothing seemed more unlikely before *Normann's* discovery than that this catalytic method should be available for the saturation of fats and oils.

Papers by *Moissan* and *Sabatier* are relied upon by the Plaintiffs in two ways: first, because *Sabatier* is referred to in the Specification, and *Moissan* is referred to by *Sabatier*, and it is said that this is an express reference by the Patentee adding to the information given by the Specification all the information to be gleaned from these Papers, and in them, it is said, are to be found directions how to prepare your catalysts for *Normann's* invention; and, secondly, it is said that, at all events, what was contained in them was public knowledge, and the hypothetical competent chemist was bound to supplement the Specification with the knowledge acquired from *Sabatier*.

The first contention is, in my judgment, untenable. It may perhaps be permissible for a Patentee to say in his Specification: — "For "the purpose of carrying my invention into effect, I refer you to such "and such a publication in which you will find all necessary directions." I doubt if this would fulfil his obligations to the public, but, at all events, on turning to the publication indicated, you must find in clear and precise terms the very process which he claims, or one which, without further experiment, can be applied for the carrying into effect of his invention. To turn the hypothetical chemist loose into the labyrinth of long chemical papers dealing with a variety of subjects more or less connected with the matter in hand, and tell him to search for himself and adopt for the purposes of the invention what he deems applicable, would be to fall altogether short of his duty as patentee. On the question of common knowledge, I think there must be shown something more than the fact that there has been recently published information which, though not directed to the matter in hand, ought, if properly understood and digested, to have led the inquirer to adopt certain methods and precautions in carrying out the invention with regard to which the Specification is silent. But further, if every line of *Moissan* and *Sabatier* were read, I do not

think it would lead the inquirer to suppose that any particular method of preparing the oxide for the purposes of *Normann's* process was necessary, nor indeed, as the experiments show, was it. *Moissan's* Paper is a description of an isolated demonstration of the reduction of a sesquioxide of nickel prepared in a particular way through various transformations down to metallic nickel, and is referred to by *Sabatier* in a Paper but remotely bearing upon *Normann's* invention. It is true that *Moissan* declares that the resulting metallic nickel will be pyrophoric, but it appears to me that there is no direct connection between a metal being pyrophoric (that is, being in a state in which it will oxidise in ordinary temperature at a white heat) and being a catalyst which can be relied upon to realise successfully *Normann's* invention. Indeed, the fact that some of the catalysts used by Mr. *Ballantyne* and Mr. *Hehner* in unsuccessful experiments were pyrophoric, seems conclusive on this point. I think, therefore, the question of how to prepare a finely-divided metal so that it may be pyrophoric is not relevant to the present case.

I come to the conclusion, upon the evidence, that *Normann's* process will not produce the result he claims for it unless the fine nickel powder is obtained in a special manner not indicated by the Specification, or unless a very strong current of hydrogen is used, and mechanical stirring or some other special device is resorted to. The possible effect of violent agitation in keeping the surface of the catalyst free from the poison of the oil is pointed out by Mr. *Ballantyne.* No hint of such a necessity is to be found in the Specification, and I think the hypothetical chemist was entitled to suppose that the process described in the Specification was sufficient to effect its purpose, and, having applied that process and failed to produce the result, was entitled to consider himself misinformed, without resorting to experiment to see in what manner the directions failed. The discovery was entirely new and contrary to anticipation, and the process described by *Normann,* for all that was generally known on the subject, might very well have been sufficient. There was no reason to presume any necessity to add to the directions, which he gave, anything from the stock of common knowledge. What appears to me very strong confirmation of the insufficiency of the Specification is to be found in the evidence of Dr. *Lewkowitsch,* a great authority on the subject. Dr. *Lewkowitsch* had endeavoured himself to obtain the saturation of oleic acid by the use of nickel as a catalyst and had failed. He afterwards became acquainted with *Normann's* Specification, and tried a further series of experiments with no greater success. He had obtained his catalyst from a solution of sulphate of nickel.

He afterwards read some further Papers by *Sabatier*, published in 1905, recommending amongst other things the use of nitrate in place of sulphate of nickel, and pointing out that nickel lost its catalytic properties if exposed to too high a temperature. With these hints, Dr. *Lewkowitsch* recommenced his experiments, and after several years succeeded in solving the problem. It is said for the Plaintiffs, and truly said, that sulphur was known to be what is called a poison to a catalyst and that therefore sulphate of nickel ought not to have been employed, but the precipitate was properly washed, and there was, in 1903, no reason to suppose, if this was done, that sulphur to an injurious extent would remain. Moreover, no warning is given in *Normann's* Specification against the use of sulphate of nickel, or as to the temperature to be employed in reduction. The evidence in this case shows that a catalyst prepared from the sulphate may be successful, and also that nickel may be heated to a red heat without destroying its catalytic properties. Certain passages in subsequent publications of Dr. *Lewkowitsch* have been referred to as discounting the evidence given by him in this action. It seems to me that they do not diminish the weight of his testimony. Here was a chemist, having special acquaintance with the subject, who tried a method of saturating oleic acid, identical with that described by *Normann*, and failed, studied *Normann's* Specification and, after repeated experiments, again failed, and, after receiving what he says was a clue from a publication by *Sabatier* in 1905, succeeds only then after experiments extending over several years. So that we find a chemist of exceptional qualifications, deeply interested in the subject, failing for years, after repeated experiments, and careful study of *Normann's* Specification, to achieve what I am asked to believe any competent chemist could, in 1903, have achieved by following *Normann's* directions, without any experiment at all.

In this connection I cannot but remind myself that, though the Patent was taken out in 1903 and purported to reveal a process of immense commercial value, no evidence has been called to show that anyone succeeded in taking advantage of the discovery for a considerable number of years after its publication; that the only evidence of sufficiency is the evidence of eminent chemists who essay to prove by experiments in 1912 that the directions contained in the Specification were in 1903 sufficient to ensure success.

I come to the conclusion that the directions in *Normann's* Specification were insufficient; and I infer, both from the evidence before me, and the lack of evidence, that, great as the discovery that unsaturated fatty acids and their glycerides could be hydrogenated by the catalytic

method undoubtedly was, no practical means of taking advantage of the discovery were disclosed until after further experiment subsequent to the date of the Patent.

It has been repeatedly urged that, catalysis depending upon contact, the difference between success or failure is simply a question of obtaining or failing to obtain contact. In my opinion, the evidence fails to establish this in any material sense. There is nothing to show that the directions of *Normann* do not suffice to get contact. Catalysis remains a mystery to-day, and in 1903 nothing whatever was known as to the means necessary to obtain successful contact in the catalytic hydrogenation of oleic acid, or any other fatty acid or glyceride, except what was disclosed by *Normann* himself. According to Mr. *Ballantyne's* evidence, a catalyst which succeeded in getting "contact" in this sense with acetylene after *Sabatier*, failed with *Normann's* process. To say that a direction to pass a strong current of hydrogen through a mixture of fine nickel powder and oleic acid, in order to expose the acid to the action of hydrogen and the catalytic substance, connotes the resort to every device known to science for making the exposure as complete or as frequent as possible, seems to me extravagant.

I therefore come to a conclusion adverse to the Plaintiffs' contention upon their own case; but I do not concur in the construction of the Specification put forward on their behalf. It has been contended that this is a Patent for a principle, and that if the Patentee shows one way of carrying it out he is entitled to claim for all ways. If *Normann* had invented the hydrogenation of oleic acid by help of a nickel catalyst, and had given sufficient information in the instance stated to ensure success, then I think he could rightly claim all other ways of arriving at the result; but here he claims to have invented a method of obtaining hydrogenation of all unsaturated fatty acids and their glycerides, and if his method fails in any one case I think his Patent would be bad. Moreover, he claims to be able to secure the result by the use of finely-divided platinum, iron, cobalt and copper as well as nickel, and if the use of any one of these catalysts is fatal to his process I think his Patent is bad.

There are other matters arising in the action which, having regard to the view already expressed, are not necessary for the decision of the case; but I may say that I think that the evidence shows that the temperature at which hydrogenation is attempted is material, not only with regard to time occupied in obtaining the desired reaction, but for obtaining such reaction at all. It may be that one element of success is the mixture of oxide of nickel with the metal. Dr. *Liebmann's* experiments, were with reduction at a low temperature, 300° to 320°

for a short period, one hour, while Mr. *Hehner* in the experiments referred to reduced at 360° for three hours. I think the evidence shows that the temperature and time employed by Dr. *Liebmann* cannot be relied upon to obtain complete reduction. It will be observed that both Dr. *Liebmann* and Dr. *Passmore*, when seeking to demonstrate that catalysts prepared in a manner similar to that adopted by the Defendants' witnesses could be used, not only in all cases resorted to stirring, but used a much larger current of hydrogen than that used in previous experiments. Having heard the evidence upon the point, I will add that, could *Normann's* Patent have stood, in my judgment, the Defendants would have infringed it.

In the result, I am of opinion that the Plaintiffs' action fails and must be dismissed with costs.

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